THE SYNTHESIS and FINE STRUCTURE STUDIES

of

POLYCYCLIC AROMATIC HYDROCARBONS

T H E S I S

presented by

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for the degree of

DOCTOR OF PHILOSOPHY

of the

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I would also like to thank Dr. B.A. McAndrew who initiated the work in Chapter 3 and Dr. R.B Mallion for a private communication of his unpublished results which appear in Chapter 6.

Finally, I am glad to have this opportunity to thank my parents for their unfailing encouragement and support throughout the course of my education.

PUBLICATIONS

The following papers have been published or are about to be published:

1. The Location of Double Bonds in Methyl-Acenes.

   E. Clar and C.C. Mackay.

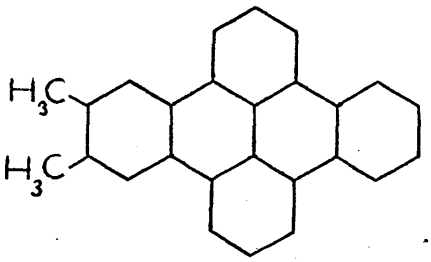
   Tetrahedron Letters, 11, 871 (1970).

2. Kekulé Structures and the Benzylic Coupling of o-Dimethyl-Derivatives.

   E. Clar and C.C. Mackay.

   Tetrahedron, in press.

C O N T E N T S



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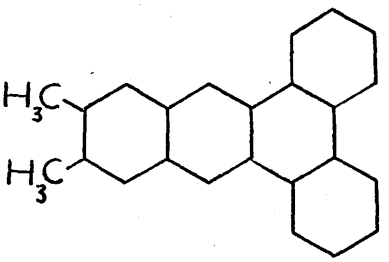

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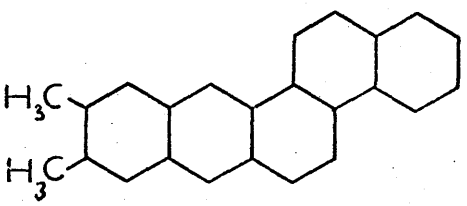

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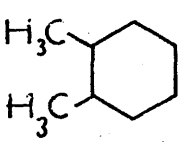

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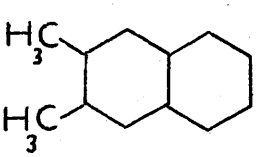

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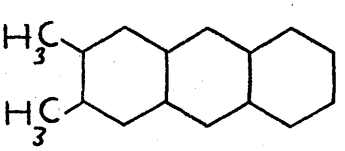


(VI)

J_{CH_3-H} = 0 Hz

J_{CH_3-H} = 0.5 Hz.

J_{CH_3-H} = 0.65 Hz.

SUMMARY

The main part of this thesis has dealt with benzylic coupling in a large number of methyl derivatives of polycyclic aromatic hydrocarbons.

It has been shown previously that a coupling constant of ~1.0 Hz. between the methyl protons and the ortho aromatic proton is indicative of a high degree of localisation and double bond character in the intervening bond. This idea has been extended by examining a series of symmetrical o-dimethyl derivatives which involved synthesising 2',3'-dimethyl-1,2:6,7-dibenzopyrene, (I) and 6,7-dimethyl-1,2:3,4-dibenzanthracene (II). 9,10-Dimethyl-3,4-benzotetraphene (III) was obtained as a by-product in the latter synthesis. The couplings in these derivatives add further evidence to the idea that there is only one true double bond in each ring which occupies the lowest energy orbital. The remaining 4 π-electrons are divided into two higher energy levels with one pair remaining delocalised within the ring, and the third pair, in the highest level, delocalised outside the ring and capable of migrating from ring to ring.

An annellation effect is thus observed in passing from o-xylene to 2,3-dimethylanthracene (IV)(V)(VI) which can be explained by the

increased linear annellation reducing the influence of those delocalised π-electrons which are free to migrate, as they are spread over more rings.

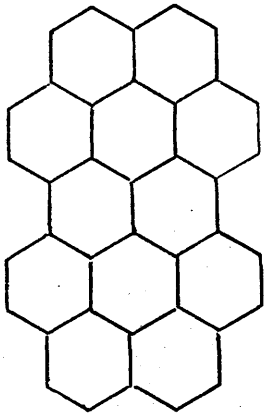
The distribution of the true double bond can also be considerably affected by substitution in the ring. This is reflected by considerable changes in the magnitude of the benzylic coupling and supports the additivity of only one true double bond in each ring.

The electronic arrangement in pyridazine is in the opposite sense to naphthalene and anthracene. There is a high degree of double bond character in the 4,5 position and a correspondingly low value in the 3,4 and 5,6 positions. This is borne out on examination of a number of methylpyridazines and adds further evidence to the above ideas.

Finally, the unusual asymmetry of the methyl resonance in α-methyl derivatives was investigated. During this work an explanation was published on the basis of computer analysis of the methyl signal and it appears that the asymmetry is inherent with this combination of couplings to the ortho, para and meta protons on the ring.

The apparent lack of long-range coupling in aromatic hydrocarbons has been attributed to 2nd order interactions. In this work halogen derivatives of anthracene and tetracene were examined. Decoupling indicates the absence of para coupling between the protons on non-terminal rings, although there is substantial trans-peri coupling between the protons of a terminal and non-terminal ring.

However a methyl group on a non-terminal ring is found to be strongly coupled only to the para proton with J= 0.8-1.0Hz. This



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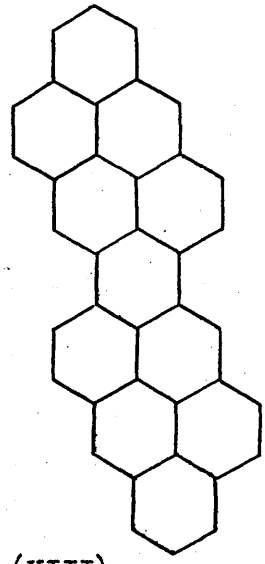

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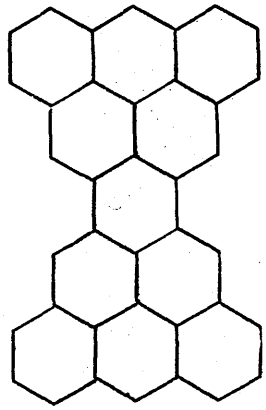

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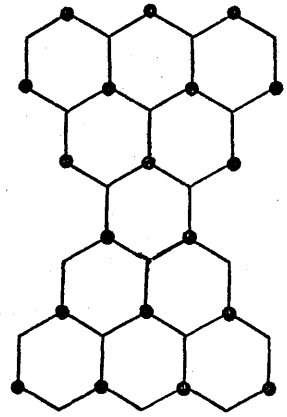


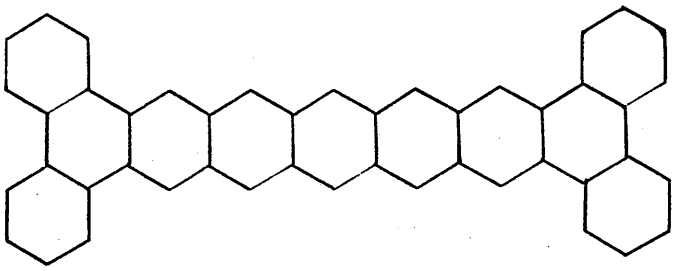
(IXa)

value is as large as the coupling constant observed for the localised double bond in 9-methylphenanthrene 1.0 Hz. This evidence is compared with other methyl derivatives and several possible explanations are discussed.

The reductive dimerisation of 6-naphthanthrone yielded the known hydrocarbons, dinaphtho-(7',1':1,13):(1",7":6,8)-peropyrene, dinaphtho-(7',1':1,13):(1",7":9,11)-peropyrene and 2,3-trimethylenepyrene along with two new hydrocarbons (VII) and(VIII). Circobiphenyl (VII) is a highly condensed hydrocarbon which can be considered as a double coronene. The U.V. spectrum is similar to coronene, however its low solubility has proved a stumbling block in efforts to obtain the n.m.r. spectrum. It was hoped that the protons of this molecule would resonate at low field thus indicating a "superaromaticity" effect analogous to coronene.

A new purple hydrocarbon was also obtained and U.V. evidence favours the structure dibenzisoviolanthrene (VIII). Application of Robinsons aromatic sextet to this structure does not indicate any localised dienophilic regions and therefore this molecule should not react with maleic anhydride. Contrary to expectations, two-fold addition of maleic anhydride does occur in a similar manner to 2,3:4,5:8,9:10,11-tetrabenzoperylene and on this basis the possibility of structure (IX) cannot be excluded.

However closer examination of structure (IX) shows that a complete Kekulé structure is not possible, despite the fact that alternant marking predicts an equal number of marked and unmarked carbon atoms. The former finding leads to the theoretical prediction of a diradical or higher structure with an inherent instability as shown by



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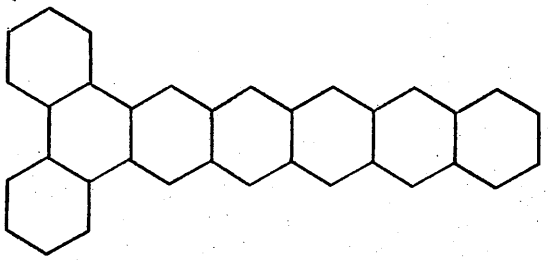

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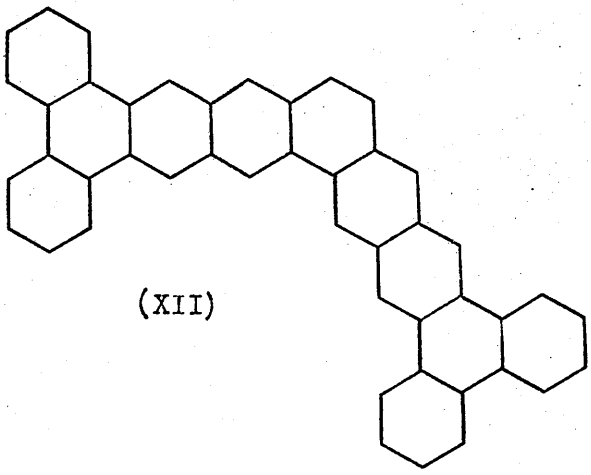


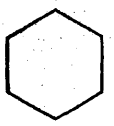
(XII)

triangulene, yet from the alternant marking scheme (IXa) a bond across the middle ring involving electrons of opposite spin might be possible. In order to test the above predictions and to try and clarify the reactivity of the purple hydrocarbon with maleic anhydride, an unambiguous synthesis of (IX) was attempted.

A series of examples which show the asymmetric annellation of two diphenyl complexes to an acene have been built up over the years. Two of the remaining members of this series are 1,2:3,4:11,12:13,14-tetrabenzheptacene (X) and 1,2:3,4-dibenzhexacene (XI). A synthesis of the former compound was undertaken to increase the scope of the above series and in an effort to obtain a reasonably stable heptacene derivative. Instead of the required compound (X), the isomeric 1,2:3,4:11,12:13,14-tetrabenzheptaphene (XII) has been isolated and its spectra and properties compared with heptaphene. Preliminary attempts to synthesise (XI) are also described.

Finally, various theoretical treatments have been put forward to explain and calculate the low field resonance of aromatic protons, and there is now good agreement between observed and calculated chemical shifts.

In this work the spectra of a number of large polycyclic aromatic hydrocarbons have been analysed. A comparison with the recent calculated chemical shifts has been made, with particular interest in the overcrowded bay protons which tend to exhibit anomolous behaviour.



(i)

(ii)

All Hexagons (i) symbolise aromatic rings. Double bonds, and Robinson's aromatic sextet (ii) which symbolises strictly 6π-electrons, are only used if some special significance is intended.

CHAPTER I.

KEKULÉ STRUCTURES and the BENZYLIC COUPLING of METHYL DERIVATIVES of POLYCYCLIC AROMATIC HYDROCARBONS.

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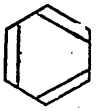
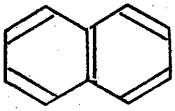
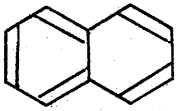


(Ib)



(IIa)



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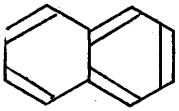


(IIc)

Introduction.

Kekulé initially explained the unsaturation of benzene by having three fixed double bonds within the benzene ring (Ia). However the failure to find the isomeric o-disubstituted benzenes inherent in this structure prompted him to extend this idea. He postulated that the double bonds were not fixed, that structure (Ib) was equally possible and that the double bonds were in fact oscillating around the ring.

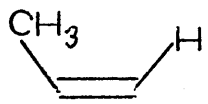
Extension of this idea to naphthalene (II) requires that the double bonds should oscillate between the three possible structures (II a,b,c). However a large amount of chemical evidence has been accumulated to show that there is a remarkable difference between the two positions ortho to a β-naphthalene substituent and that the 1 position is almost invariably preferred in a reaction.[1] This infers that the double bonds are located in the 1,2 and 3,4 positions rather than the 2,3 position in naphthalene, and that the double bonds are not as mobile as in benzene, but rather fixed in the symmetric structure (IIa).

However when chemical reactions are applied in these efforts, the inherent difficulty is that an excited state rather than the ground state of the molecule may be participating.

With the advent of n.m.r. spectroscopy, a new physical method was made available for studying the molecule in its electronic

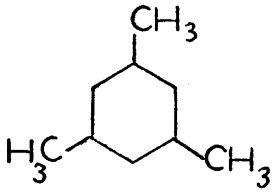
ground state. In the earlier years, the proton chemical shift appeared to be the most important source of information available to organic chemists. However with the development of more sophisticated instruments, offering better resolution of individual nuclear resonance signals, the phenomenon of spin-spin coupling between neighbouring nuclei became increasingly important. This offers a direct measurement of the long-range interaction between the individual protons, as opposed to the chemical shift which indicates the immediate electronic and magnetic environment of the protons on the molecule.[2] Complementary to spin-spin coupling, the extremely useful technique of double irradiation spin decoupling was developed. By independently irradiating the sample at the specific frequency of an individual proton resonance, one can effectively remove the spin-spin interaction of that proton with all the other protons to which it is coupled, while still observing the remainder of the spectrum. Thus in cases of a molecule with a complicated spectrum, double irradiation can often simplify the spectrum and allow a more detailed assignment of the proton resonance signals.[3]

In our particular work we have dealt with the long range spin-spin coupling of the aromatic protons with the methyl group in a series of methyl substituted polycyclic aromatic hydrocarbons and their derivatives. Before reviewing our findings in more detail it is worth considering the spin-spin coupling constants



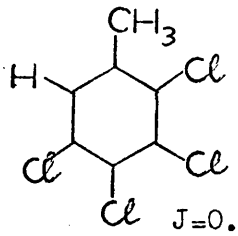
J=1.7 Hz.

(III)



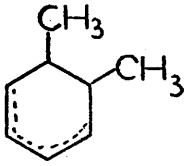
J=0.6 Hz.

(IV)



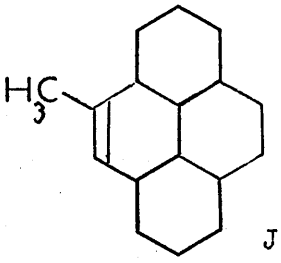
J=0.6 Hz.

(V)



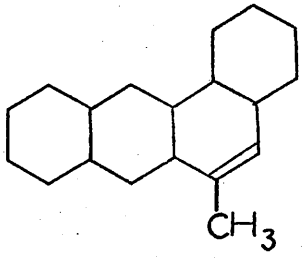
J= 0 Hz.

(VI)



J=1.1 Hz.

(VII)



J=1.1 Hz.

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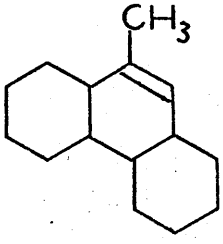

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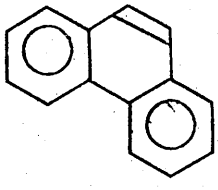

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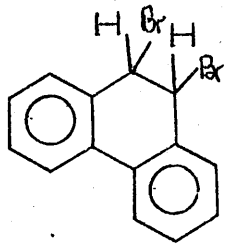
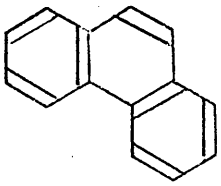


(XI)

of what might be termed the two extreme cases, namely the $J(H-C=C-CH_3)$ of a simple alkene system and the equivalent coupling constant as found in a suitably substituted benzene. The magnitude of the coupling in propene (III) show J=1.6 - 1.8 Hz.,[4,5] while in the latter case dealing with an aromatic compound, such as 2,3,4,5-tetrachlorotoluene (IV) and mesitylene (V), J = 0.6 Hz.[6] Thus we have a comparison between the coupling in a fully localised double bond in the propenes and the delocalised system as in mesitylene or the substituted toluene.

However extensive study of a large number of methyl derivatives has shown that the situation is more complex. The value of J_{CH_3-H} can vary from zero (at least not measurable by present day instruments) in o-xylene (VI) to as high as 1.0 -1.1 Hz. in 1-methylpyrene[7] (VII) and 4-methyltetraphene (VIII)[7,8] and almost 1.0 Hz. in a suitably substituted toluene. The magnitude of the couplings gives an indication of the degree of double bond character in these positions.

Initial investigation by Clar and coworkers showed that in 9-methylphenanthrene (IX) the large coupling 1.1 Hz. between the methyl group and the proton, H_{10} indicated a considerable degree of double bond character in the 9,10 position.[6,7] This was backed up chemically by the smooth addition of bromine at the 9,10 positions of phenanthrene (X) forming the reasonably stable 9,10-dibromo-9.10-dihydrophenanthrene (XI). In all hydrocarbons investigated to-date with a methyl substituent in a similar 'angle' position, the magnitude of the coupling is $\sim$ 1.0 Hz.



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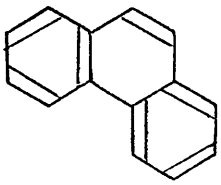
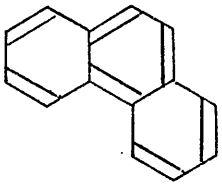


(XIIb)



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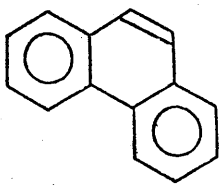

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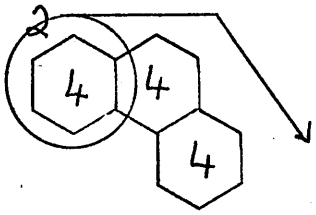

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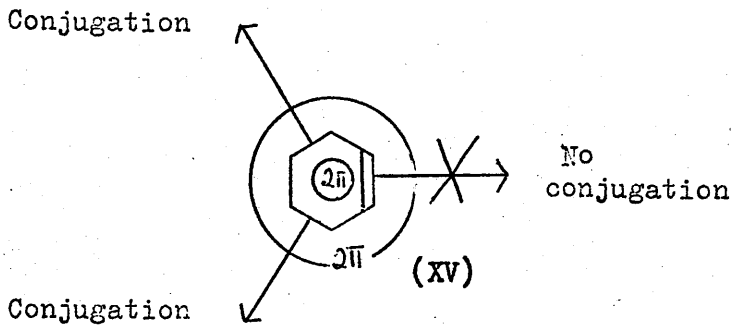

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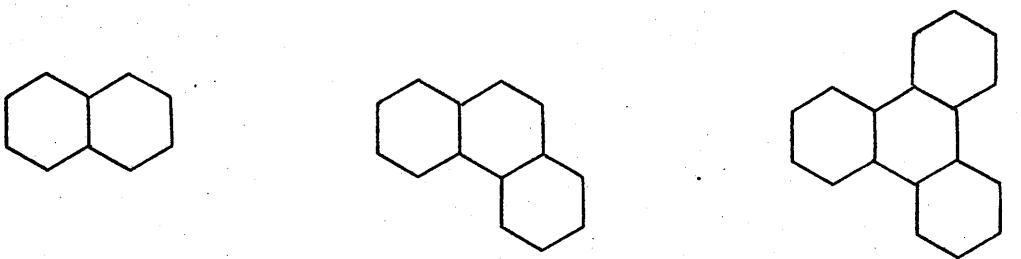
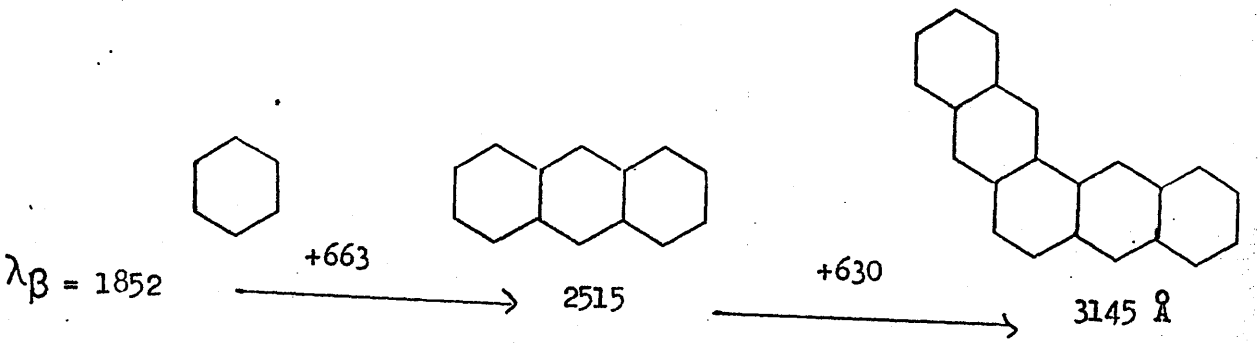
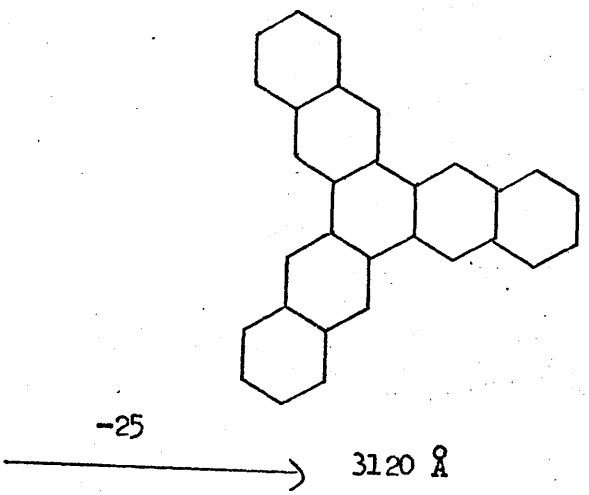


Series (XVI)

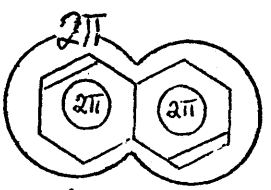
On consideration of the arrangement of π- electrons in phenanthrene in more detail, writing conventional Kekulé structures one can have the possible arrangement shown. In structures (XIIab) the terminal rings each have three pairs of double bonds and can be considered as inherent sextets, leaving the remaining double bond localised in the 9,10 position (XIII). A more uniform distribution is obtained if two electrons from the highest level of one sextet fill the second level in the middle ring, as shown by transformation of structure (XIII) into (XIV). The remaining π- electrons are therefore free to migrate over all the rings. This offers an explanation for the conjugation of the system, while retaining localisation of the double bond in the 9,10 position and explaining the reactivity at this position (X).

Further evidence for this idea has been derived from the observation of the non-existence of three-fold conjugation in linear benzologues of pentaphene and in cases of the 1,2;3,4-dibenzacenes.[9] Very simply this showed that only two branches of the molecule were involved in conjugation, during the time of light absorption. The explanation of this phenomenon involves the idea of having the localised double bond in the lowest level in the middle ring thus cutting off conjugation to the third branch and allowing only twofold conjugation at any particular instance (XV). Thus annellation of a ring to the 9,10 position of phenanthrene, or the 5,6 position of pentaphene forming a third branch in the molecule causes only small violet shifts in the





Series (XVII)



(XVIII)

U.V. spectra, series (XVI) and (XVII), as this third branch does not contribute overall to the conjugation. This is shown even more dramatically in the starphenes.[10] From heptaphene to decastarphene only small violet shifts are observed despite the fact that the third branch consists of three linear rings, which would cause a huge red shift if linearly annellated to an acene. Fig. I.

The extension of this idea to all benzene rings results in a subdivision of the aromatic sextet. One pair of π -electrons is located in a true double bond, the pair in the next highest level are delocalised within the ring and the third pair delocalised in an orbital outside the ring, are capable of migrating from one ring to the next (XVIII).[10]

It is hoped to show from the following n.m.r. evidence that the splitting of the methyl signal in methyl derivatives of polycyclic aromatic hydrocarbons can be related to this idea of having only one true double bond in each ring. This double bond is not necessarily fixed, the distribution within the ring can be affected by substitution in the ring and an additivity principle accounting for only one true double bond can be inferred.

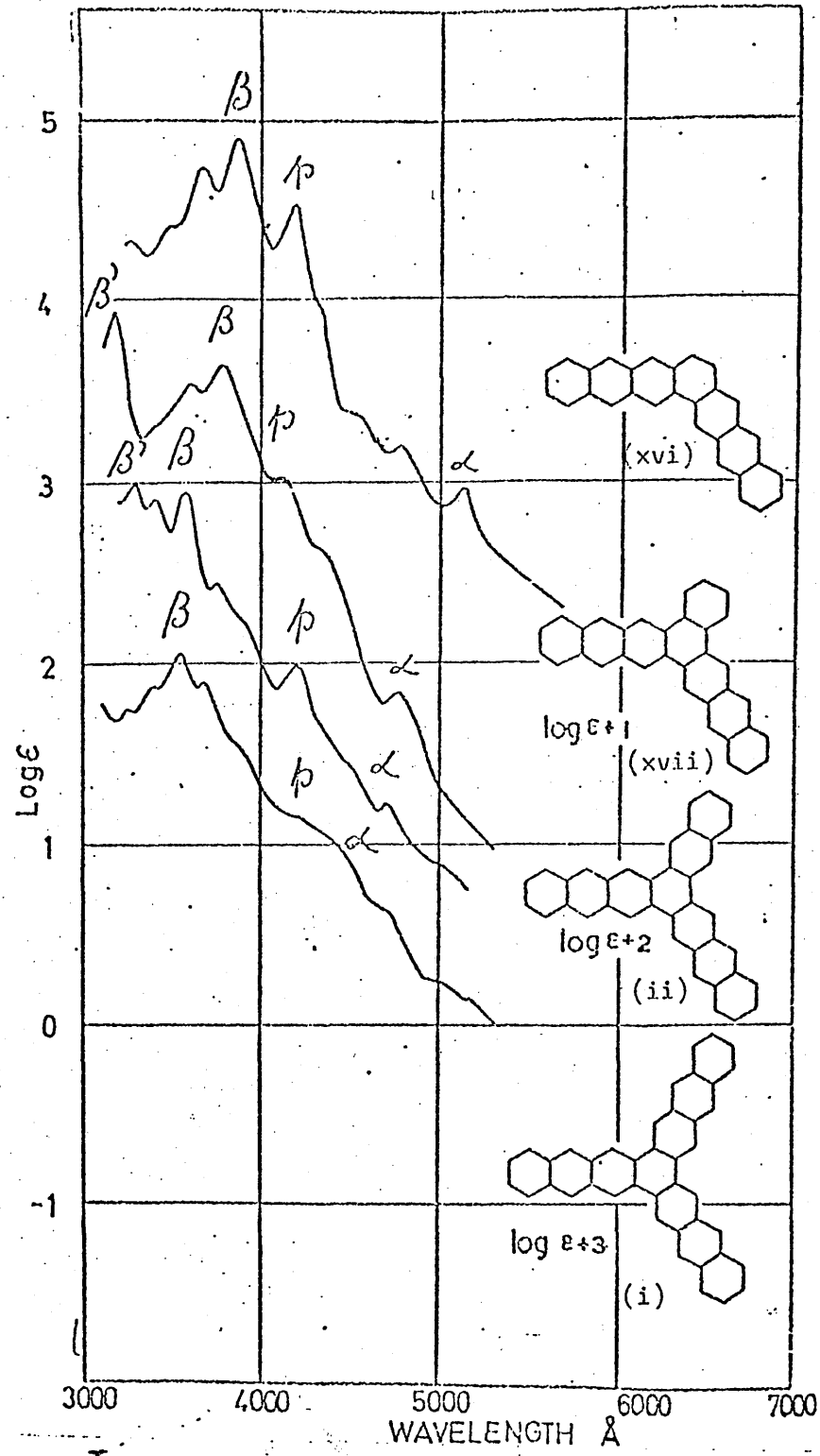


FIG. I Absorption spectra in trichlorobenzene with max (Å) and log ε in (parentheses).
Heptaphene: α: 5190 (2·94), 4870 (3·16), 4570 (3·34); p: 4220 (4·47); β: 3900 (4·83), 3700 (4·67).
Octastarphene-(1,3,3): α: 4850 (2·82); p: 4170 (4·02); β: 3840 (4·60), 3660 (4·49); β': 3220 (4·88),
Nonastarphene-(2,3,3): α: 4·700 (3·22); p: 4200 (3·99); 3760 (4·44); β: 3590 (4·95), 3420 (4·90); β': 3310 (4·99).
Decastarphene-(3,3,3): α: 4700 (3·66)?; p: 4250 (4·08)?; 3670 (4·89); β: 3540 (5·04), 3380 (4·88).

Section 1. Benzylic Coupling in Symmetrical o-Dimethyl and other Methyl Derivatives.

Discussion

The methyl signal of o-xylene (I) Fig. 1 is a sharp singlet which is little affected by decoupling of the aromatic protons as shown in Fig. 1. A true double bond could only be located in the positions 3,4,5,6. This non-adjacent double bond in o-xylene becomes apparent in 4,5 - dibromo-o-xylene II Fig. 1 where the methyl signal is a doublet with a separation of 0.3 Hz. This can be explained by a structure as shown in Fig.1.

Extension to polymethylated benzene nuclei complicates matters as an asymmetrical arrangement of the methyl groups causes intermethyl coupling, which although small tends to broaden the signals with a corresponding loss of resolution. However the symmetrical molecule durene (III) Fig. 1 has a methyl signal with a splitting of 0.3 Hz. and since this results from two three-centre bonds the degree of localisation must be rather high in these positions (III) Fig. 1.

The methyl signal of 2,3 - dimethylnaphthalene (IV) Fig. 1 is a rather clear doublet with a separation of 0.5 Hz. Decoupling of the protons H_1 and H_4 produces a sharp singlet. Substitution of H_1 by a bromine atom increases the separation

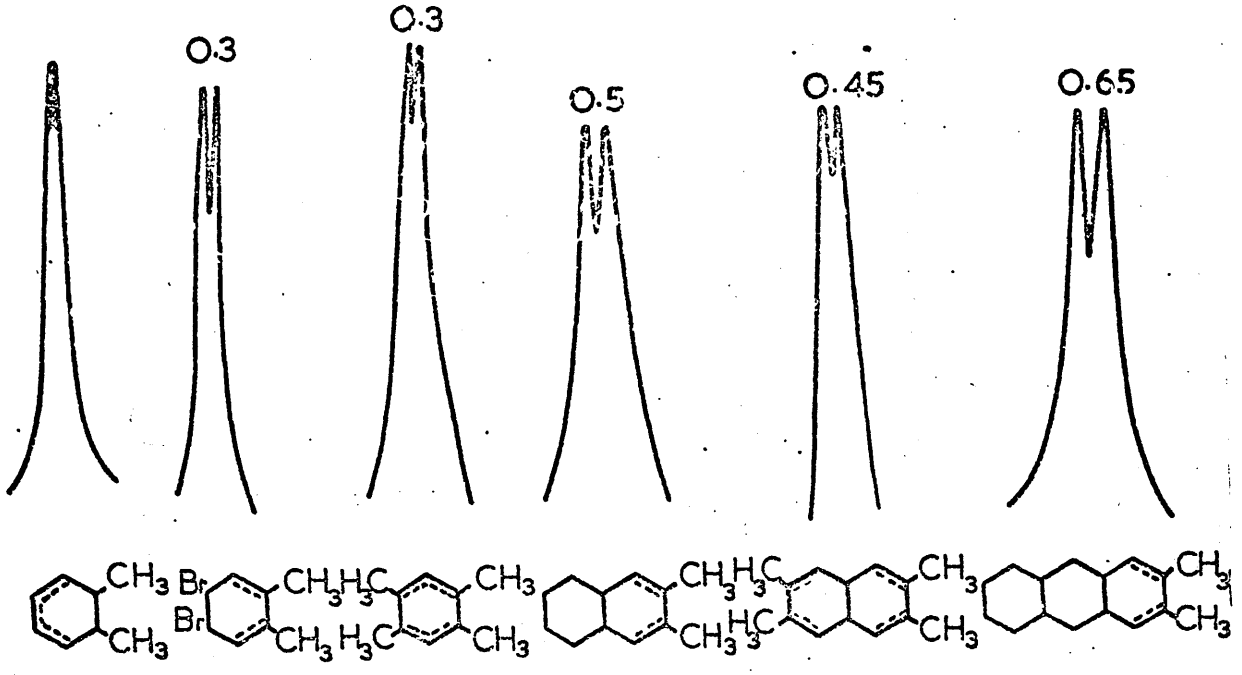
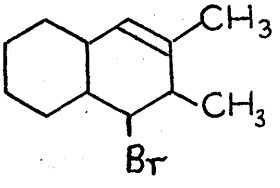


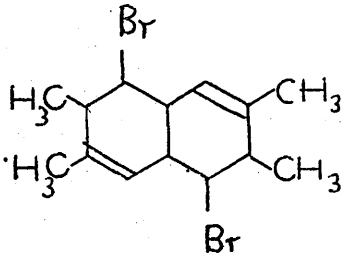
Fig. I

Comparison of the CH_3 signals from the n.m.r. spectra of symmetric di- and tetramethyl derivatives.



(IVa)

$J_{3\text{-}CH_3,H_4}$=0.9Hz



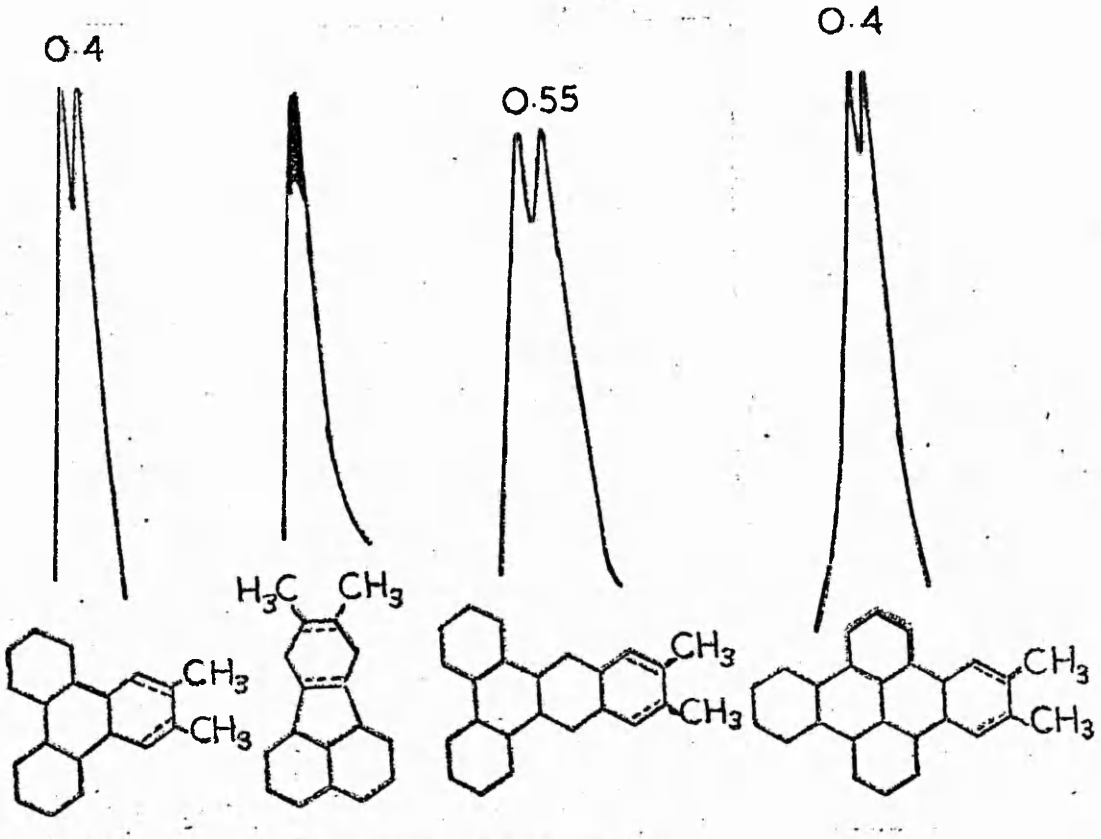
(Va)

$J_{3\text{-}CH_3,H_4}$ = 0.7 Hz

to 0.9 Hz. This example (IVa) shows the additivity of true double bond character which is the result of repulsion of part of one true double bond by the large electron cloud of the halogen. This cannot be explained by Kekulé structures.[11]

To investigate whether the same situation arises in the second ring, the spectrum of 2,3,6,7 - tetramethylnaphthalene (V) Fig.1 was recorded. The single methyl resonance is indeed a doublet, but the separation of 0.45 Hz . is certainly less than in 2,3 - dimethylnaphthalene (IV) Fig. 1. It may be reasonable to assume that those circular delocalised π- electrons which can migrate through both rings are to some extent localised into the unsubstituted ring in 2,3 - dimethylnaphthalene thus making the substituted ring less benzenoid and more reactive. This cannot be the case in 2,3,6,7 - tetramethylnaphthalene and one must conclude that these circular delocalised π-electrons have a slight counteracting effect to the tendency to localise the true double bond adjacent to the β-methyl groups.

Correspondingly, the same effect is observed in 1,5 - dibromo - 2,3,6,7 - tetramethylnaphthalene (Va). The low field methyl signal is singlet, the high field methyl signal is a doublet with a separation of 0.7 Hz This reduction in the splitting of the methyl signal compared with 0.9 Hz observed in 1 - bromo - 2,3 - dimethylnaphthalene (IV) confirms the findings in the parent hydrocarbons.



(VII) (VIII) (IX) (X)

Fig.2 Comparison of CH_3 signals from the n.m.r. spectra of symmetric dimethyl derivatives.

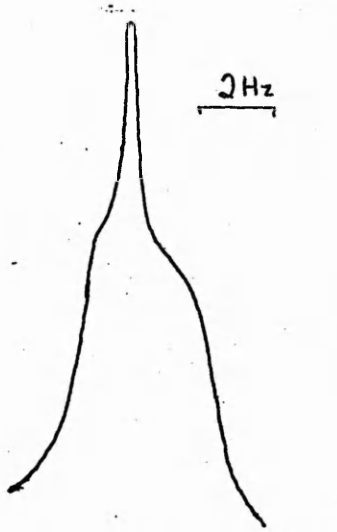
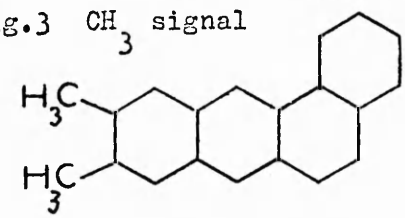
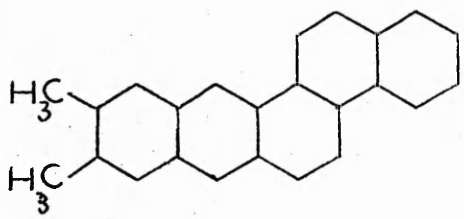


Fig.3 CH_3 signal



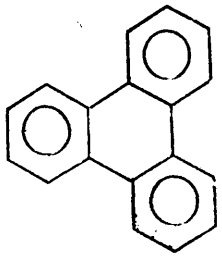
(XI)



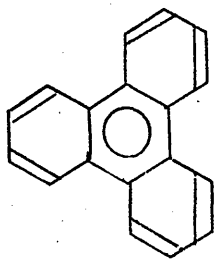
(XII)

This being the case the influence of the circular delocalised π- electrons must be further reduced in 2,3 - dimethylanthracene (VI) Fig. 1 which as expected has a methyl doublet with a larger separation of 0.65 Hz. In passing from benzene to naphthalene and anthracene derivatives a distinct annellation effect is thus observed.

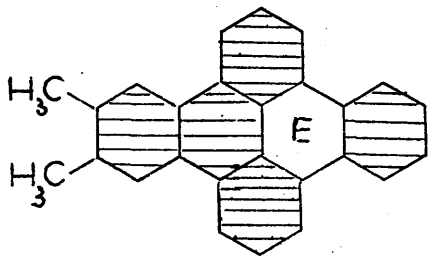
Up to this point only the effects of linear annellation on the magnitude of the methyl splittings have been discussed and it seemed worthwhile to consider the effects of angular annellation. However examination of the methyl resonance of 6,7 - dimethyl-tetraphene (XI) and 9,10 - dimethyl - 3,4 - benzotetraphene (XII) showed that the asymmetry of the molecule gave rise to two methyl signals with such similar chemical shifts that the smaller long-range couplings were not detectable. The methyl signal of (XI) in particular had an extremely odd shape as indicated in the figure 3 : apparently a triplet arising from the superposition of the two methyl doublets. Decoupling the protons H_5 and H_8 gave rise to the individual methyl signals with a chemical shift difference of only 0.013 p.p.m. However, the single methyl signal of the symmetrically substituted 2,3 - dimethyltriphenylene (VII) Fig. 2 shows a separation of 0.4 Hz. This value is lower than in 2,3-dimethylnaphthalene (0.5 Hz.) and 2,3,6,7 - tetramethyl-naphthalene (0.45 Hz.), yet slightly greater than in dibromo-o-xylene and durene (0.3 Hz.).



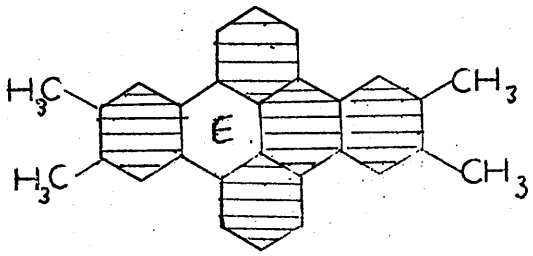
(XIII).



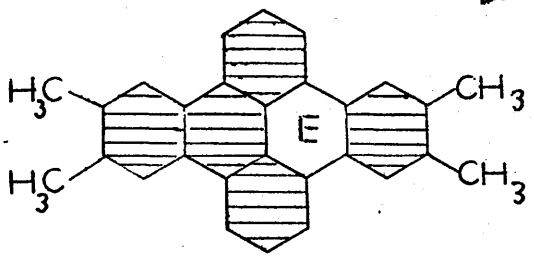
(XIIIa)



(Xa)



(Xb)



(Xb)

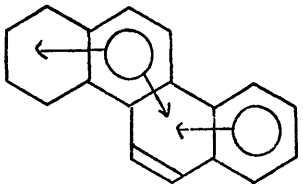
Triphenylene is best formulated with three aromatic sextets in the external rings as can be seen from the diagram (XIII). The alternative structure with the middle ring an inherent sextet does not seem feasible as it only has one sextet (XIIIa).[12] There is also evidence from diamagnetic anisotropy measurements which demonstrate clearly that the electron density in the central ring amounts to only half of an aromatic ring.[13] It is therefore understandable that the splitting of the methyl doublet is between the above mentioned benzene and naphthalene derivatives.

Returning to the annellation effect observed in the acene series, the methyl doublet of 6,7 - dimethyl - 1,2;3,4 - dibenzanthracene (IX) Fig. 2 has a separation of 0.55 Hz. This is indeed larger than the splitting in 2,3 - dimethyltriphenylene (VII) Fig. 2 yet is smaller than the value recorded for 2,3 - dimethylanthracene 0.65 Hz. The effect of the linearly annellated ring has increased the splitting passing from 2,3 - dimethyltriphenylene to 6,7 - dimethyl - 1,2;3,4 - dibenzanthracene, yet the effect of angular annellation to the 1,2 and 3,4 positions of the anthracene derivative has reduced the value, just as in going from 2,3 - dimethylnaphthalene to 2,3 - dimethyltriphenylene.

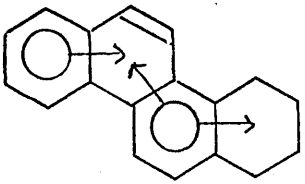
The magnitude of the splitting in 2,3 - dimethyltriphenylene can be usefully applied when considering the spectrum of 2',3' - dimethyl - 1,2;6,7 - dibenzopyrene (X) Fig. 2. The methyl signal is a doublet with a separation of 0.4 Hz. which is exactly the

same value as recorded for 2,3-dimethyltriphenylene. This leads to the assumption that the aromatic conjugation of the triphenylene complex (marked with shadow) and an empty ring "E" dominate the electronic structure of this molecule (Xa). If both methyl groups were connected to the phenylene ring adjacent to the empty ring "E", then no splitting of the methyl signal should be observed as in o-xylene. In the case of the electronic structure resonating between these two structures, the methyl splitting should be halfway between 0 and 0.4 Hz, which is obviously not the case. This asymmetric electronic structure for 1,2:6,7-dibenzopyrene and its higher benzologues has already been deduced from the electronic spectra.[14] It is interesting to speculate what the magnitude of the splitting would be in 2',3',2",3"-tetramethyl-1,2:6,7-dibenzopyrene (Xb) in the light of the methyl signals of 2,3-dimethylnaphthalene and 2,3,6,7-tetramethylnaphthalene. One would certainly expect a value which would be about halfway between 0 and 0.4 Hz. if each structure contributed equally. Otherwise one would have two individual methyl signals, a singlet for the o-xylene part, and a doublet with J=0.4 Hz. for the triphenylene part. The former explanation certainly appears most likely, but the problem remains unsolved.

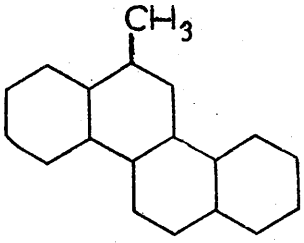
Having dealt with symmetrically substituted dimethyl derivatives of molecules with only hexagonal rings it is interesting to compare the results with those of fluoranthene derivatives which contain



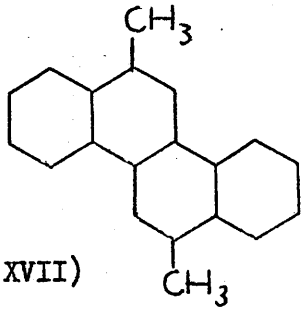
(XVa)



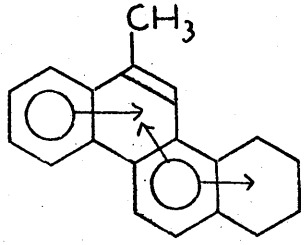
(XVb)



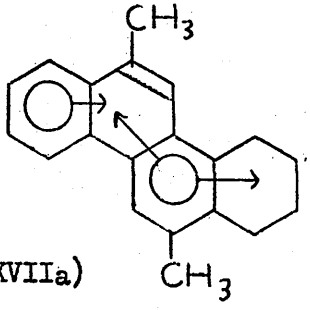
(XVI)



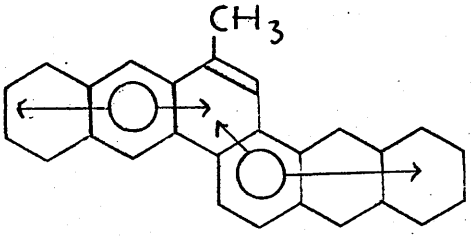
(XVII)



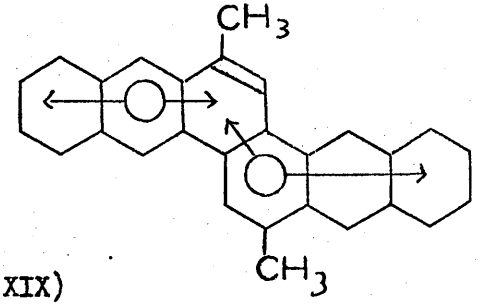
(XVIa)



(XVIIa)



(XVIII)

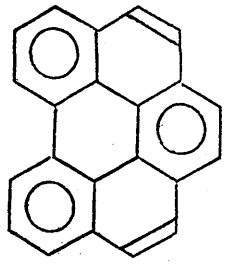


(XIX)

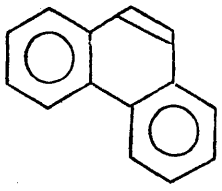
a five membered ring. No splitting can be observed in the methyl signal of 8,9-dimethylfluoranthene (VIII) Fig. 2. Decoupling of the adjacent aromatic protons, H_7 and $H_{8'}$ has very little effect as shown by the black area.[15] One must therefore assume a similar electronic structure for the ring attached to the methyl groups as in o-xylene. This appears even more reasonable, since 7,10-dimethylfluoranthene (XIV) also shows no methyl doublet but a rather sharp singlet, very little affected by decoupling of the protons H_8 and H_9.[15] In this case the ring with the methyl substituents must be closely related to p-xylene.[11]

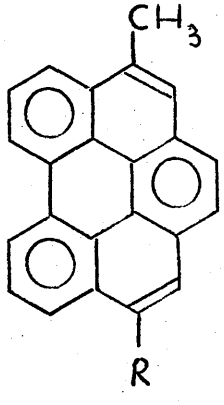
Another striking example which contributes to the idea of diminution of the splitting of the methyl resonance by the circular delocalised π-electrons is found in chrysene. Chrysene can best be formulated with two sextets free to migrate as shown (XVa,b). 2-Methylchrysene (XVI) shows the characteristic methyl doublet with a splitting of 1.1Hz.,[7] for a molecule with the methyl attached in an "angle" position. This means that the best formulation to explain the size of the splitting is as indicated (XVIa) with a phenanthrene type double bond. Expansion of the methyl doublet of 2,8-dimethylchrysene (XVII) shows a separation of only 0.7 Hz. which is substantially less than the value observed for the monomethyl derivative. This was previously thought to be a broad singlet due to poor resolution.[7]

However although 2-methylchrysene (XVIa) can readily adopt



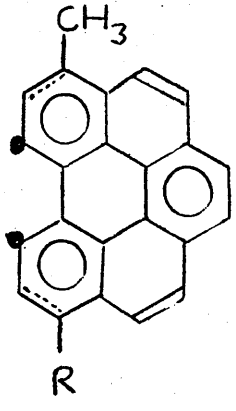
(XX)





(XXI), R = H

(XXII), R = CH_3



(XXIII), R = H

(XXIV), R = CH_3

● Decoupled

a phenanthrene type of structure with a fixed double bond this is not possible for both methyl groups in the dimethyl derivative. Each methyl in turn will be attached to a ring which is effectively an inherent sextet, while the other methyl is attached to a phenanthrene type of double bond. (XVIIa). The net result is a compromise situation in which there is a correspondingly smaller splitting of the methyl signal, the result of the average of two extremes. This is repeated in the analogous series 4-methyl-anthraceno-(2',1':1,2)- anthracene (XVIII) and 4,4'- dimethyl-anthraceno-(2',1':1,2)-anthracene (XIX) where the splitting of the methyl signals are 1.1 and 0.85 Hz. respectively, although the former compound is very insoluble and the spectrum is difficult to record. This smaller difference in splitting between the monomethyl and the dimethyl compound also fits well, as the circular delocalised π-electrons are now spread over more rings and an annellation effect similar to that observed for benzene, naphthalene and anthracene is repeated.

A further confirmation of this general idea can be made by considering the methyl derivatives of 1:12-benzoperylene.[16] The parent compound, 1:12-benzoperylene is best formulated with three inherent sextets, as shown (XX) with two induced sextets and localised double bonds in the 2,3 and 10,11 positions, exactly as found for phenanthrene. The methyl signals of both 3-methyl and 3,10-dimethyl-1:12-benzoperylene (XXI,XXII) are

clear doublets with a separation of 1.1 Hz.[16] The corresponding methyl signals of both the 4-methyl and 4,9-dimethyl derivatives (XXIII,XXIV) are broad singlets. However decoupling of the protons H_6 and H_6 , H_7 in the meta positions (marked with dots.) produces a doublet with a separation of 0,6 Hz. This clearly shows that the 2,3 and 10,11 bonds are similar to the middle 9,10 bond of phenanthrene with a high degree of double bond character indicated by the large coupling constant, while the remaining rings must be inherent sextets.[16]

The overall electronic arrangement in 1:12-benzoperylene is therefore fixed and the sextets are not free to migrate. Therefore the monomethyl and corresponding dimethyl derivatives have exactly similar methyl signals as they are both in the same electronic environment, unlike the monomethyl and dimethyl derivative discussed in the previous examples.

It is difficult to explain the above results on the basis of rigorous Kekulé structures with three double bonds, but they can be rationalised to a large extent, by assuming there is only one true mobile double bond in each benzenoid ring. This would be placed in the lowest orbital of the three π-orbitals and its distribution can readily be influenced by substitution in the ring as will be shown in the following section.

Section 2. The Effect of Substituents on the Observed Couplings in Methyl Derivatives.

Discussion

As stated already the methyl signal of o-xylene(V)Fig. I is a singlet, and that of 4,5-dibromo-o-xylene (VI) Fig. 1, a doublet with a separation of 0.3 Hz. As shown, p-xylene (III) Fig. 1 also shows a sharp singlet methyl signal and decoupling the aromatic protons has very little effect. 2,5-Dibromo-p-xylene (IV) Fig. 1 has a methyl signal which is just starting to split with a separation of 0.2 Hz. Localisation in this case does not appear to occur to the same extent as in dibromo-o-xylene. m-Xylene (VII) Fig. 1 is a less symmetrical molecule and correspondingly the aromatic protons are no longer a single signal. The methyl resonance is a deceptively simple quartet, with a mean splitting of 0.5 Hz. 4,6-Dibromo-m-xylene (VIII) Fig. 1 shows a quartet methyl resonance resulting from ortho and meta coupling with the aromatic protons. Decoupling of the proton H_5 , produces a sharp doublet with a separation of 0.65 Hz. (VIIIa) Fig. 1. In this case there must be a high degree of localisation in the three centre bond (VIII,VIIIa).

It was also shown earlier that the methyl signals of 2,3-dimethylnaphthalene (IX) and 2,3-dimethylanthracene (X) were distinct doublets with separations of 0.5 and 0.65 Hz.

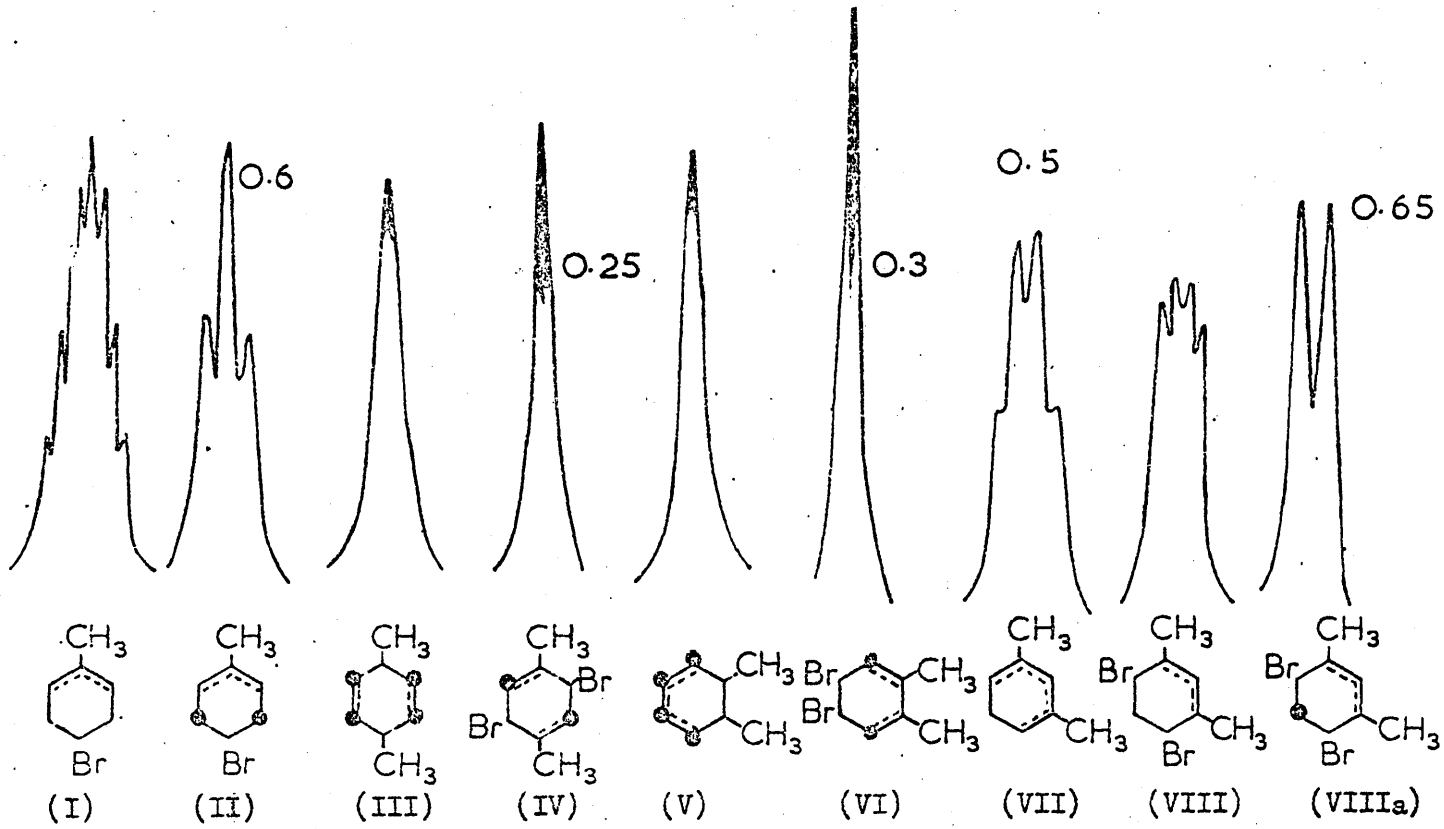


Fig 1. Comparison of the methyl signals from the N.m.r. spectra of p-xylene, o-xylene, m-xylene, p-bromotoluene and their bromo derivatives.

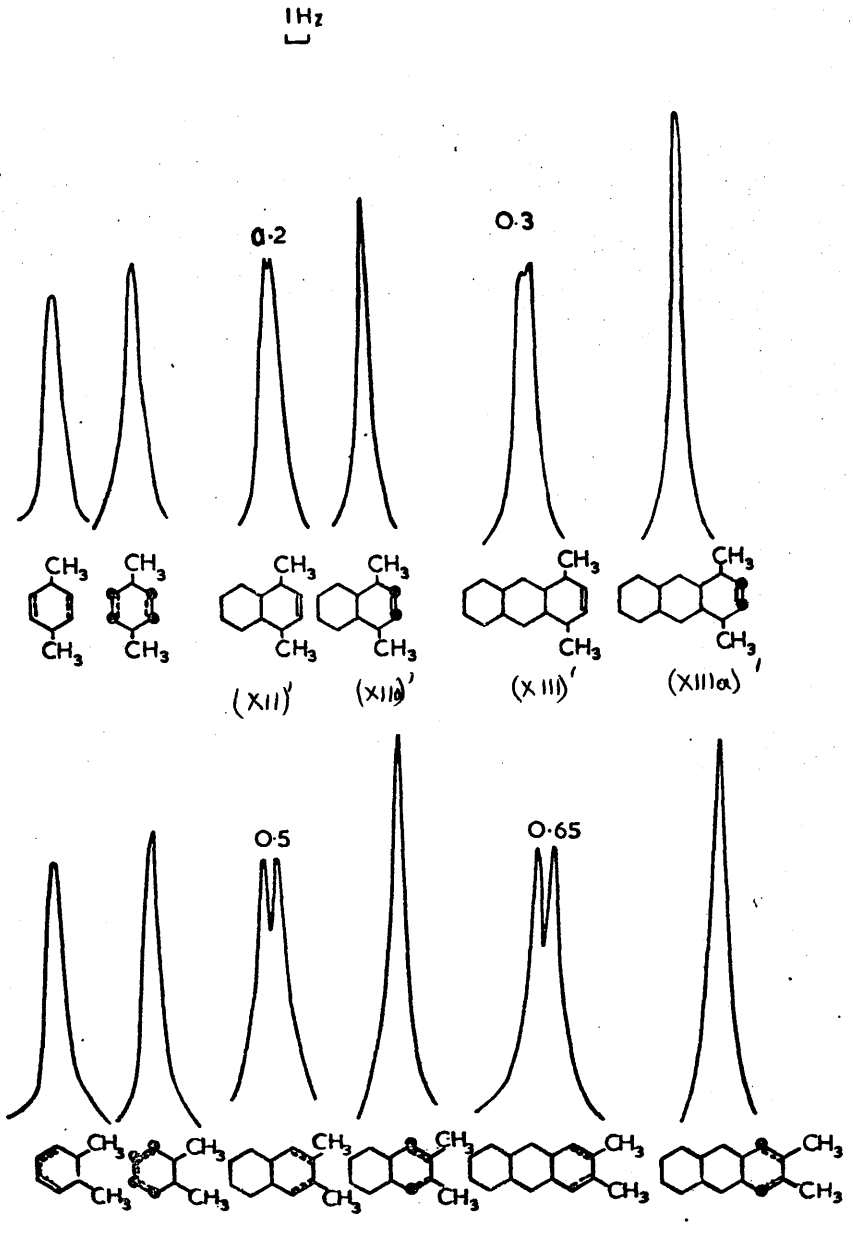
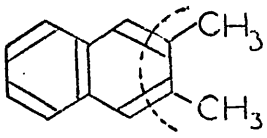
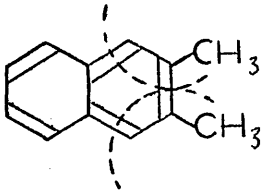
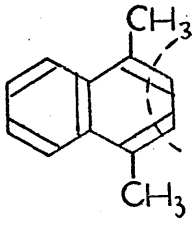


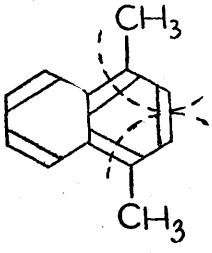
Fig. 2. CH_3 NMR signals of p-xylene, 1.4-dimethylnaphthalene, 1.4-dimethylanthracene, o-xylene, 2.3-dimethylnaphthalene and 2.3-dimethylanthracene at 60 MHz in CS_2. Decoupled protons are marked with points.





	Dimethylglyoxal	:	Methylglyoxal
Expected value if both structures contribute equally.	1	:	2
Found experimentally.	10	:	1





	Methylglyoxal	:	Glyoxal
Expected value if both structures contribute equally.	2	:	1
Found experimentally.	1	:	4

respectively, these are shown in Fig. 2. It is an amazing fact that the methyl signals of 1,4-dimethylnaphthalene (XII) and 1,4-dimethylanthracene (XIII) Fig. 2 although doublets have splittings of only 0.2 and 0.3 Hz. respectively[11]. Decoupling of the aromatic protons, H_2 and H_3 (marked by dots) also shows that the degree of coupling is very small (XIIa, XIIIa) and hardly consistent with 50% double bond character in the bond adjacent to the methyl group.[11] The electronic arrangement of the double bonds in this case must be different and a possible explanation is shown in Fig. 2 which compares the two annellation series for 1,4 and 2,3- disubstituted acenes

An interesting piece of chemical evidence which adds some weight to this idea is the ozonisation experiments of Wibaut and others[17] who investigated the distribution of double bonds in benzene and naphthalene derivatives. An 'a priori' consideration of the oxidation products of 2,3-dimethylnaphthalene would lead one to expect a yield of dimethylglyoxal and methylglyoxal in the ratio 1:2 provided all three bonds were equal in double bond character. Experimentally however this ratio is found to be 10:1. Similarly the expected ratio of methylglyoxal and glyoxal from the corresponding oxidation of 1,4-dimethylnaphthalene would by 2:1, experimentally it is found to be only 1:4. This latter case although not as convincing as the former does indicate a tendency for the arrangement shown

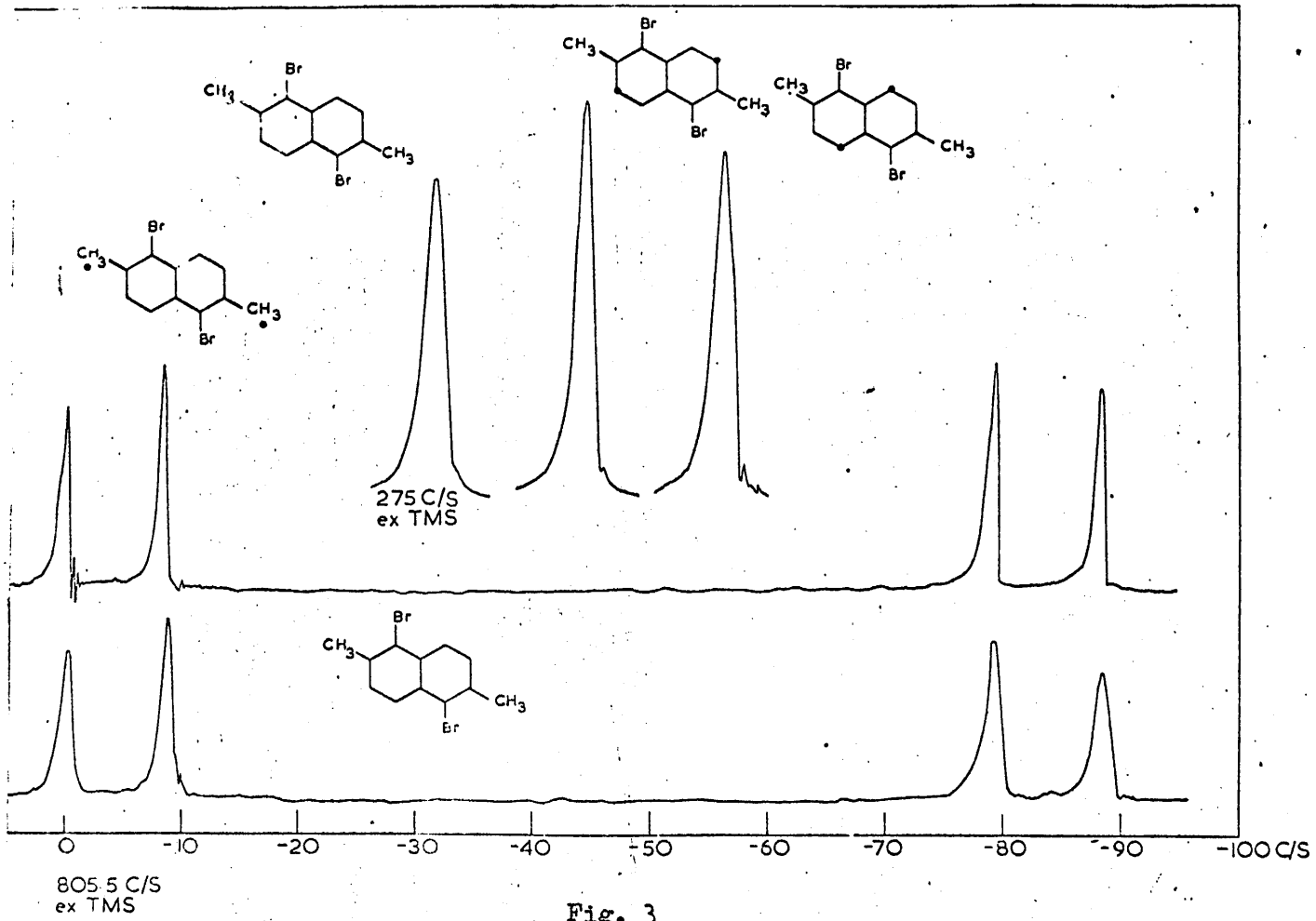


Fig. 3

N.m.r. spectrum of 1,5-dibromo-2,6-dimethylnaphthalene in CS_2 at 100MHz.

CH_3 275 ; $H_{3,7}$ 722 ; $H_{4,8}$ 800 Hz. exo TMS. $J_{3,4} = J_{7,8} = 8.7$Hz.

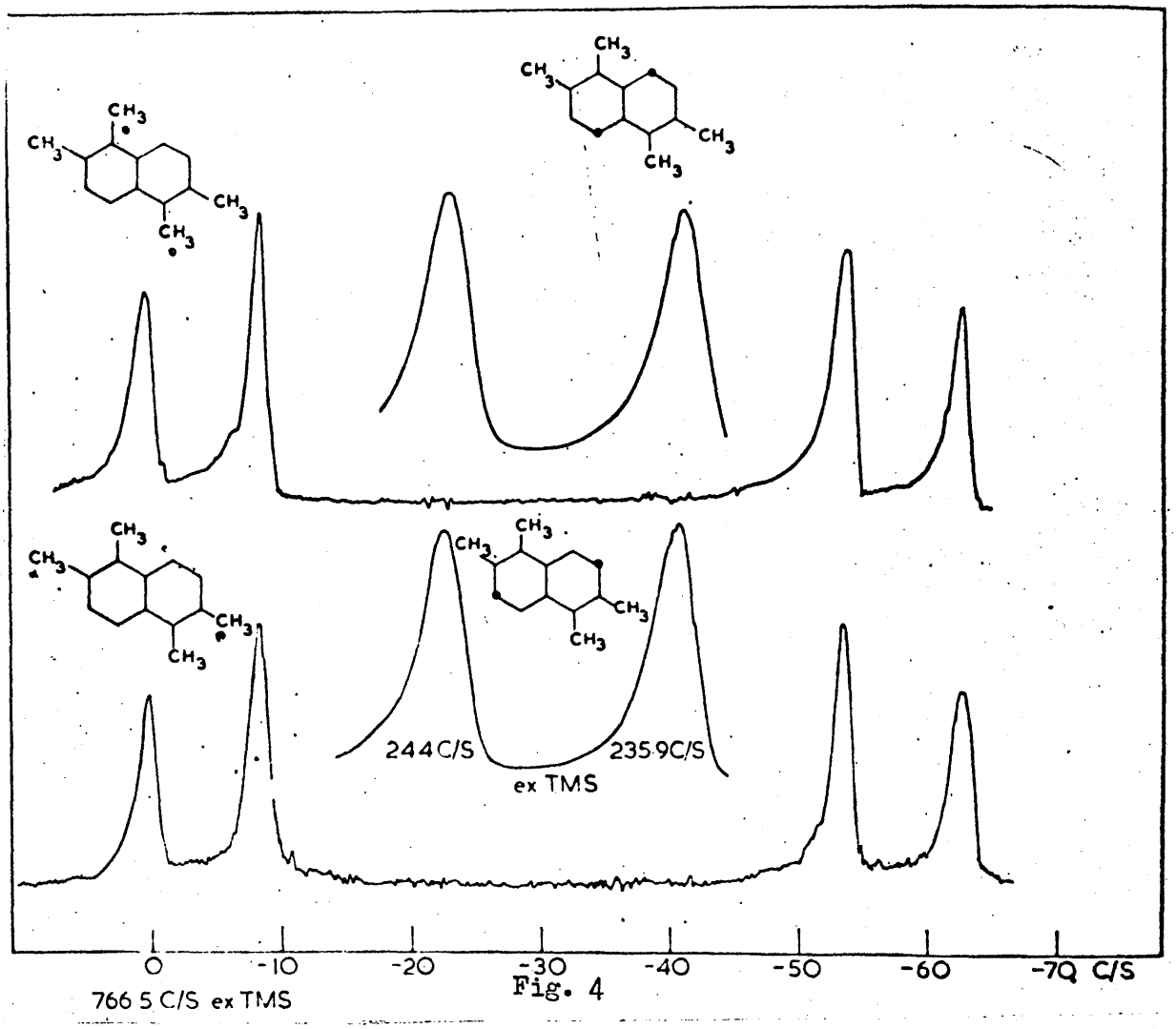
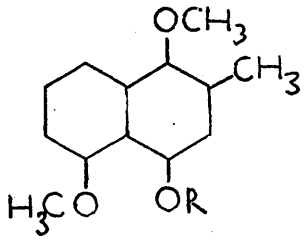


Fig. 4

N.m.r. spectrum of 1,2,5,6-tetramethylnaphthalene in CS_2 at 100 MHz. 1,5-CH_3 244 ;2,6-CH_3 236 ;$H_{3,7}$ 709; $H_{4,8}$ 762 Hz exo TMS.



(IX) R = H

R = $COCH_3$

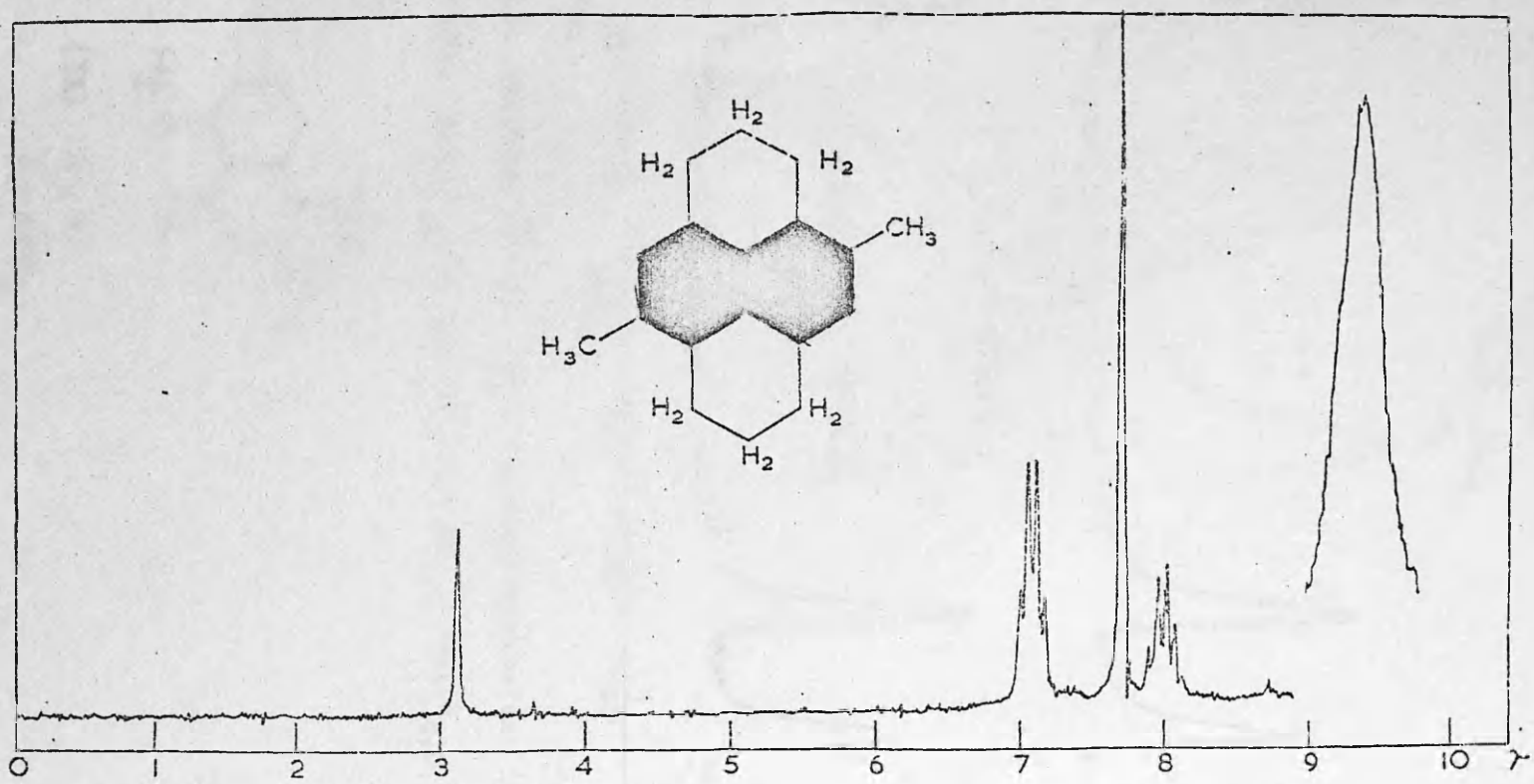
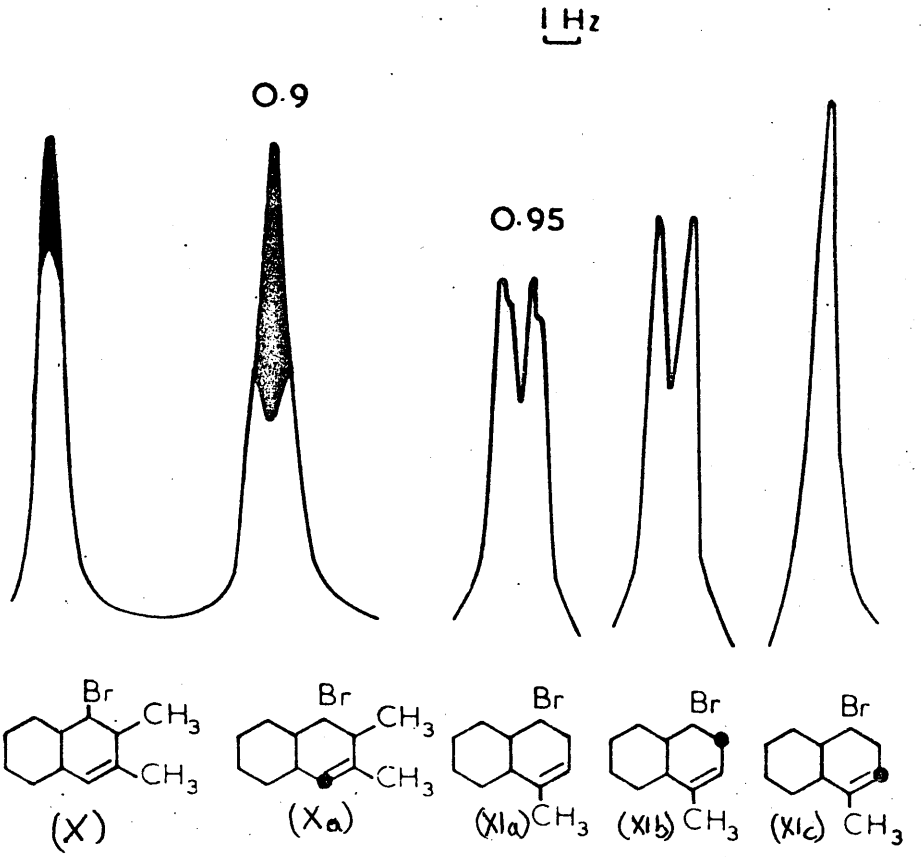


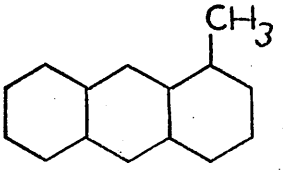
Fig 5. N.m.r. spectrum of 1,6-dimethyl-3,4,5,8,9,10-hexahydropyrene in CS_2 at 100MHz. $1,6\text{-}CH_3$ 226(s) ; $H_{2,7}$ 681 ; $H_{3,5,8,10}$ 288(m) ; $H_{4,9}$ 199(m), Hz exo TMS.

in Table 1. However one point is very clear: the methyl signal of 1,5-dibromo-2,6-dimethylnaphthalene Fig. 3 is a very sharp singlet with no evidence of coupling with the aromatic protons. Decoupling the protons H_3 and H_7 causes very little sharpening of the methyl signal and there is even less of an effect on decoupling the protons H_4 and H_8 (marked by points) Fig. 3. Therefore, there can be little or no coupling across the 2,3 or 6,7 bonds in this naphthalene derivative and it appears that the true double bond in each ring will be mostly localised in the α,β positions. This is confirmed by the spectrum of 1,2,5,6-tetramethylnaphthalene Fig. 4, in which the methyl signals although broader due to adjacent intermethyl coupling are little affected by decoupling the aromatic protons H_3, H_4, H_7 and H_8 (marked with points) Fig. 4. The above evidence can be compared favourably with the findings in 1,6-dimethyl-3,4,5,8,9,10-hexahydropyrene Fig. 5, in which the remaining aromatic part of the molecule is effectively a naphthalene complex and there is no evidence of coupling between the methyl group and the aromatic proton across the β,β position.[18] This was also shown quite conclusively in a recent paper (which will be discussed later).[19] The compound (IX) has a methyl signal which is a sharp singlet and the aromatic proton H_3 is also a sharp singlet.[19]

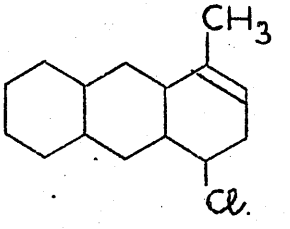
It must be concluded that there is no true double bond between the β,β positions in these naphthalene derivatives and



Fig, 6. CH_3 NMR signals of 1-bromo-2.3-dimethylnaphthalene and 4-bromo-1-methylnaphthalene in CS_2 at 60 M.Hz. Decoupled protons are marked with points; black area after decoupling.



(XIII)



(XII)

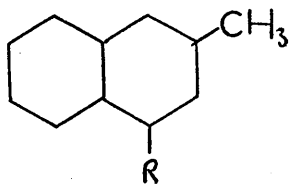
that it must be localised in the α, β positions. However this does not explain the small observed couplings in 1,4-dimethylnaphthalene and 1,4 dimethylanthracene unless there is a different electronic arrangement as suggested.

It was noted earlier that substitution of a bromine atom at the 1 position in 2,3-dimethylnaphthalene caused an increase in the coupling between the methyl substituent in the 3 position and the proton H_4, ortho to it. (X,Xa) Fig. 6. The methyl signal of 1-methylnaphthalene is an asymmetric doublet (this will be discussed later) with a splitting of the order of 0.7 Hz The corresponding signal of the methyl group in 1-bromo-4-methylnaphthalene[11] is a symmetrical doublet with a separation of 0.95 Hz. (XIa) Fig. 6. The shoulders on each arm of the doublet due to meta coupling (0.25 Hz.)can be removed by decoupling the proton H_2 (XIb) Fig. 6. The signal is also sharpened to a singlet when the proton H_3, ortho to the methyl group is decoupled (XIc) Fig. 6. This is readily confirmed by the corresponding 1-chloro-4-methylanthracene (XII). The doublet methyl signal has a separation of 1.0 Hz. compared with the asymmetric signal of 1-methylanthracene (XIII) which has a separation of 0.75 Hz. Decoupling of the aromatic protons has the same effect as described above. This new coupling between the methyl and the adjacent ortho proton is therefore much larger than the couplings recorded for either 1,4-dimethylnaphthalene or 1,4-dimethylanthracene Fig.2.

One can only conclude that by some mechanism possibly electron repulsion the halogen substituent has favoured double bond fixation as indicated in (XIa,b,c) Fig. 6.

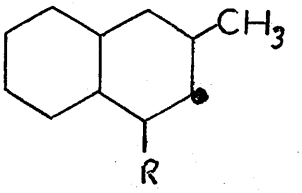
Very recently a paper dealing with double bond fixation in substituted 2-methylnaphthalene derivatives has been published.[19] The authors find that for compounds of the type shown (XIV) the methyl signal is not a doublet but a broad singlet of half width 0.5 Hz. Further substitution at the 3 position (marked with a dot) (XIV) causes the methyl signal to resonate as a doublet with a separation of 1.0 Hz. They infer from this, that a substituent in the 3 position is therefore more important in localising the double bond in the 1,2 position than a substituent in the 4 position. However, they have only dealt with derivatives with the methyl group in the 2 position and have only considered compounds in which both the 3 and 4 positions are substituted, but have not looked at a compound which has a substituent only in the 3 position. Nevertheless both approaches show that the electronic arrangement appears to be different for 1-methyl and 2-methyl substituted derivatives and that both cases are affected by additional substituents.

This is further demonstrated in derivatives of toluene. Fig. 7. The methyl signal of toluene is an unresolvable broad singlet.[20] 4-Bromotoluene (XV) produces a methyl signal which is essentially



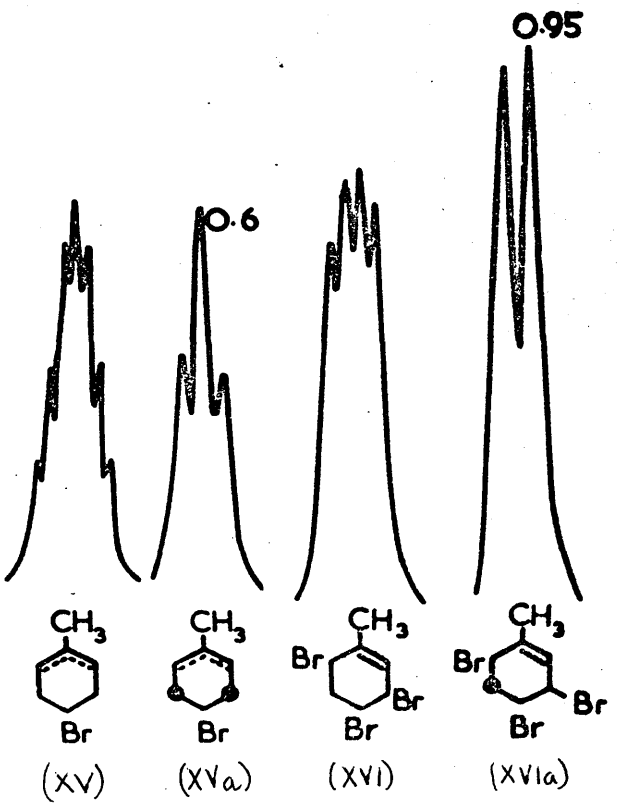
(XIV)

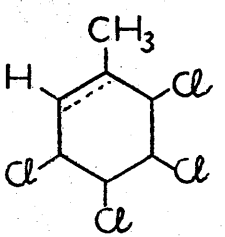
CH_3 singlet, $J_{\frac{1}{2}width}$=0.5Hz.



(XIVa)

CH_3 doublet , J_{CH_3,H_1} =1.0 Hz.





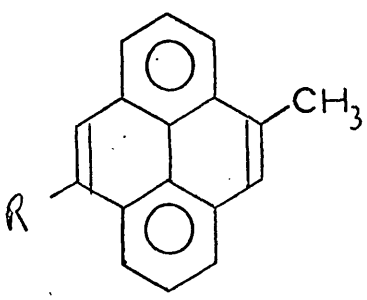
J= 0.63 Hz

Fig. 7. Comparison of the methyl signals from the N.m.r. spectra of toluene and its bromo- derivatives.

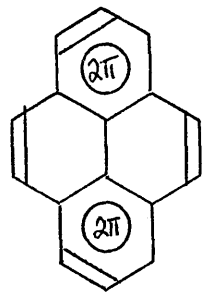
a septet produced by first order overlapping triplet of triplet. The double bond is located as a three-centre bond adjacent to the methyl as shown by decoupling of the meta protons which reduces the methyl signal to a clear triplet with a separation of 0.6 Hz. (XVa) Fig. 7. In 2,4,5-tribromotoluene (XVI) Fig. 7 the methyl signal is a clear double doublet. Decoupling of the proton H_3 which is in a position meta to the methyl group produces a doublet with a separation of 0.95 Hz. (XVIa) Fig. 7, which is the highest value yet observed in a toluene derivative[21] and is not much different from the doublet separation (1.0 Hz.) in 9-methyl-phenanthrene. This can only be explained by a high degree of localisation of the double bond between the methyl and the ortho proton.

One can conclude therefore that the electronic structure of the benzene ring is not principally different from any other benzenoid ring, only the mobility of the only true double bond is greater. If the double bond in 2,4,5-tribromotoluene is almost completely fixed then this cannot be the case to the same extent in 2,3,4,5-tetrachlorotoluene which has a methyl doublet with a separation of only 0.63 ± 0.02 Hz.[6] In this case either the chlorine atoms are not as effective in localising the double bond or (more likely) that the symmetrical tetrasubstitution does not favour complete localisation.

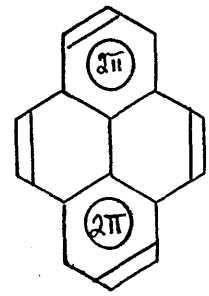
During a rigorous investigation of the electronic arrangement



(XVII) R= CH_3 or H



(XVIIIa)



(XVIII)

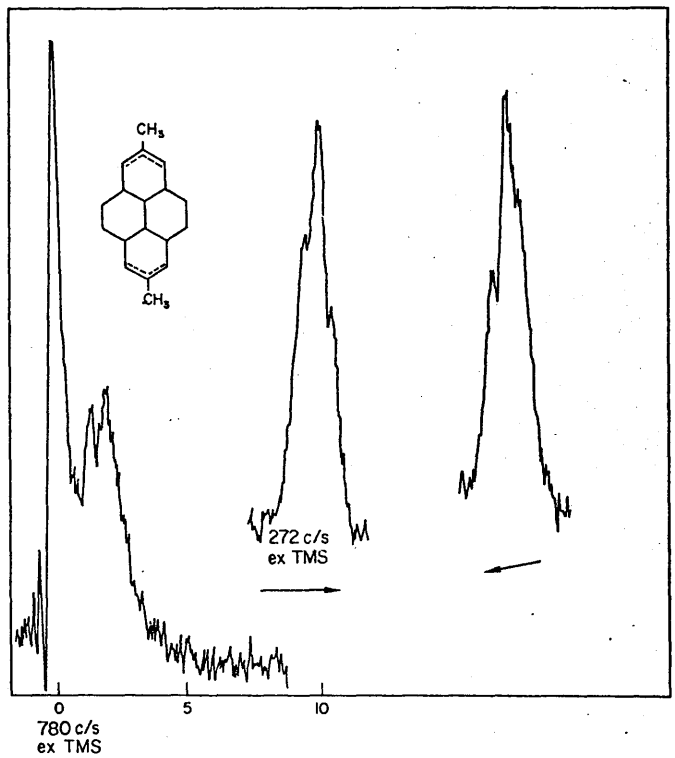
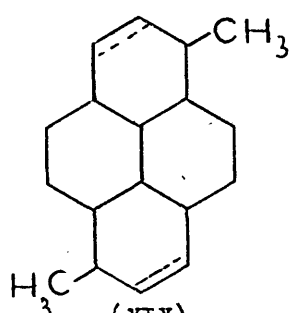
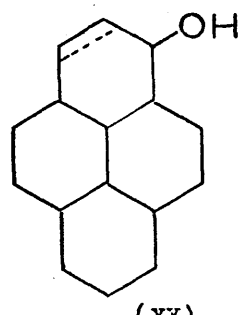


FIG 8 NMR spectrum of 4,9-dimethylpyrene in CS_2 at 100 mc/s. H_{Me}, 272·0 (triplet, separation 0·55 c/s); $H_{1,2,6,7}$, 780·0; $H_{3,5,8,10}$, 778·2 (quartet).



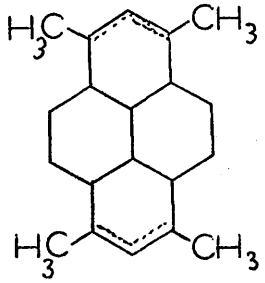
(XIX)



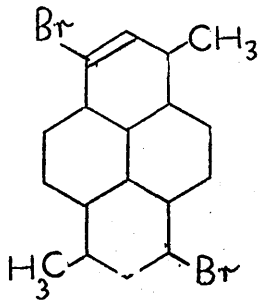
(XX)

of pyrene by Clar and coworkers,[18] it was readily shown that the 1,2 and 6,7 positions approached fully localised double bonds and methyl substituents in these positions had a splitting of 1.1 Hz. (XVII). It was also shown that the upper and lower rings which are inherent sextets contained a large degree of double bond fixation and that pyrene is best formulated in either a centro-symmetrical or a plane-symmetrical form both of which must oscillate or 'flip' to preserve the symmetry of the molecule[22] (XVIIIa,b.). 4,9-dimethylpyrene Fig.8 consequently shows a triplet methyl signal with a splitting of 0.7 Hz. This can be explained by assuming three-centre bonds over the carbons 3,4,5 and 7,8,9 or an averaging effect due to oscillation of the double bond as described . However, 3,8, - dimethylpyrene (XIX) shows a singlet methyl resonance, sharpened only slightly by decoupling of the protons H_5 , H_{10} and H_4 , H_9 , which infers that the double bond is in the 4,5 position rather than in the 3,4 position. This is confirmed by the lack of diazo coupling[23] in 3-hydroxypyrene (XXI) which has been explained by localisation of the double bond in the 4,5 position. The methyl signal of 3,8,5,10-tetramethylpyrene (XXII) is a broad doublet however, with an indistinct coupling of 0.6 Hz , which is sharpened to a broad singlet when the protons H_4 , H_9 are decoupled.[18]

It therefore seemed worthwhile to investigate 3,8-dibromo-5,10 -dimethylpyrene (XXIII) as the added effect of a bromine



(XXII)



(XXIII)

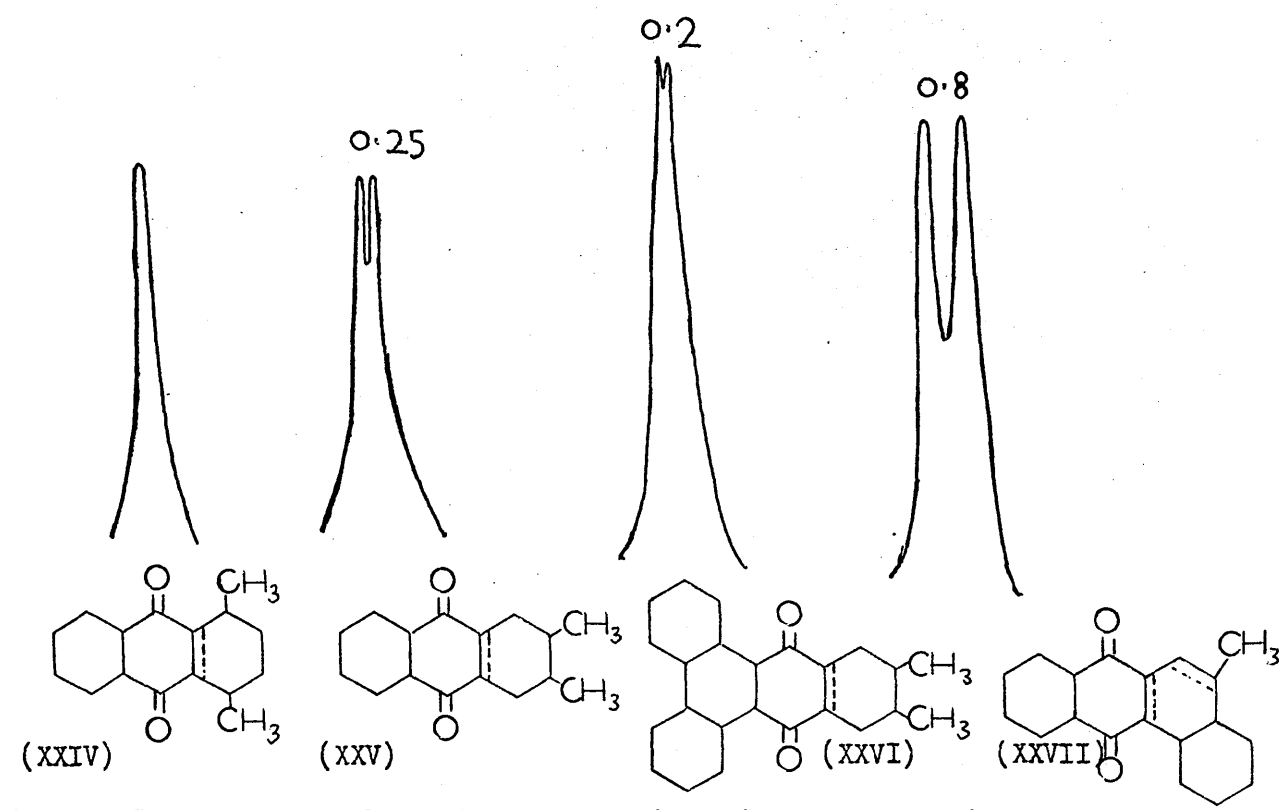


Fig.9. Comparison of the methyl signals from the n.m.r. spectra of sevaral methyl substituted quinones.

substituent might increase the double bond character in the 4,5 and 9,10 positions away from the bromine atom and adjacent to the methyl group. However, despite the effect of halogen substituents in previous examples, the methyl signal remains a broad singlet and shows no evidence for enhanced double bond character in the 4,5 or 9,10 positions. One can only conclude that the pyrene structure is better served by having the double bond localised in a position away from the methyl group or that this averaging effect in the three-centre bond distorts the methyl signal and prevents observation of a doublet.

Finally, in this section dealing with the effects of substituents on methyl derivatives of aromatic hydrocarbons the intermediate anthraquinones formed during the synthesis of the anthracene derivatives were also investigated by n.m.r. Similar parallels to the annellation effects were observed but to a much lesser degree, as the splittings were greatly reduced in magnitude. Fig.9 The methyl signal of 1,4-dimethylanthraquinone (XXIV) is a sharp singlet hardly affected by decoupling of the protons H_2, H_3, and 2,3-dimethylanthraquinone (XXV) shows a methyl signal which is a doublet with a separation of 0.25 Hz., in both cases much less than the anthracene derivatives. Similarly, 6,7-dimethylanthraquinone (XXVI) has a methyl doublet with a separation of only 0.2 Hz, and 5-methyl-1,2-benzanthraquinone has a separation of 0.8 Hz. (XXVII) compared to 0.55 Hz. and 1.1 Hz. in the

corresponding hydrocarbons. These diminished separations can be explained by a tendency for localisation of the true double bond between the electron deficient carbonyl groups as indicated by dotted lines in Fig.9 . Similarly the effect of halogen substituents in the ring is not as evident in the splitting of the methyl signal as in the hydrocarbons. 1-Chloro-4-methyl-anthraquinone shows a methyl resonance which is a double doublet. Decoupling of the proton H_3 produces a doublet with a splitting of 0.55 Hz, due to ortho coupling with the proton H_3 . This is considerably less than the value in the hydrocarbon, 1.0 Hz., and the meta coupling 0.3 Hz. although not evident when the proton H_2 is decoupled can be measured readily from the normal methyl signal. Although the parent hydrocarbon of 2-chloro-3-methylanthraquinone was not obtained the methyl signal shows exactly the same characteristics with meta coupling of 0.35 Hz. to the proton H_1 and a larger coupling of 0.55 Hz. with the ortho proton, H_4 .

Therefore the couplings between the methyl group and the aromatic protons in the quinones are diminished in comparison with the corresponding hydrocarbons. There must be a different electronic arrangement in the ring in which the true double bond is largely localised between the electron deficient carbonyl groups, thus lessening the double bond character in the α,β positions compared with the corresponding hydrocarbon.

It can be seen from the evidence above that the magnitude of the couplings and therefore the distribution of the true double bond within the rings is affected by further substitution, and the variation in the magnitude of the methyl-aromatic proton couplings appears to be very useful for detecting these changes. However although a series of substituents show a general trend, the effect of each particular substituent may have to be evaluated independently.

Section 3. Methyl Derivatives of Pyridazine.

Discussion

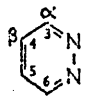
Since the splittings of the methyl signals in the quinones were so different from the corresponding hydrocarbon derivatives, it was decided to investigate a system with a known degree of localisation but in a different manner from the compounds already considered.

In fact pyridazine (I) Table 1 is very suitable for this purpose. Two analyses of the AA'XX' system of the protons of this molecule have been undertaken[24,25] and the correct couplings from the latter investigation[25] are shown. There is a high degree of double bond character in the 4,5 positions where $J_{4,5}$ = 8.6 Hz. and very much less in the 3,4 and 5,6 positions where $J_{3,4} = J_{5,6}$ = 5.2Hz., which is the opposite arrangement to that for naphthalene and anthracene.

A comprehensive study of the n.m.r. spectra of pyridazine has been accomplished by Tori and Ogata,[24] although the presentation of the results seems to have been mixed up. They investigated several methyl derivatives of pyridazine but appeared more interested in the substituent effect on the coupling and chemical

TABLE 1

Notation:

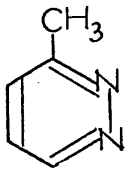


(I)

$J = J_{3,4} = J_{5,6}$
$J' = J_{5,5} = J_{4,6}$
$J_A = J_{3,6}$
$J_X = J_{4,5}$

Proton magnetic resonance parameters of pyridazine

	J	J'	J_A	J_X	τ_A	τ_B
1. Liquid	5·0	2·1	1·4	8·6	0·309	1·967
2. 20% in $CDCl_3$	5·2	1·9	1·4	8·6	0·833	2·460



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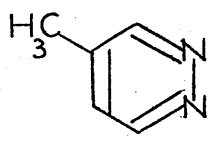

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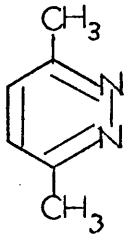

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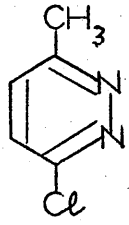

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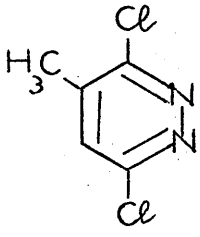


(III)

shifts of the aromatic protons. The methyl signals although recorded and expanded were not dealt with in as much detail. In this work the methyl signals have been expanded at high resolution and the decoupling technique employed.

The methyl resonance of 4-methylpyridazine (II) Table 2 is a broad multiplet which appears to be a double doublet. Decoupling the protons H_3 , H_6 produces a doublet with a separation of 1.0 Hz., in character with a high degree of double bonding in the 4,5 position. The signals of the protons H_3 and H_6 have almost identical chemical shifts and cannot be decoupled independently. They form the XY part of an AXY spectrum with the proton H_5 , but this has not been analysed. Decoupling the proton H_5 , also produce a doublet with a separation of 0.65Hz. This results from the contribution from the ortho proton H_3 , and the meta proton H_6 , but the individual effect of these protons cannot be measured separately. The A part of the aromatic spectrum is a very clear multiplet of 14 peaks due to four overlapping quartets and decoupling at the methyl frequency produces a quartet, the distance between the outer lines 1,4 gives a check on the value of $J_{XA} + J_{YA}$.[26]

The spectrum of 3,6-dichloro-4-methylpyridazine (III) Table 2 shows only two signals resulting from the methyl and the aromatic proton H_5 . The methyl signal is a doublet with a separation of 0.9 Hz. and the aromatic proton signal is a clear quartet

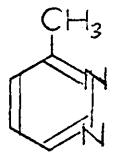
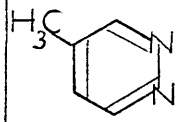
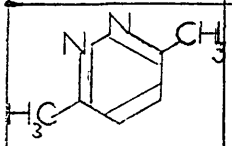
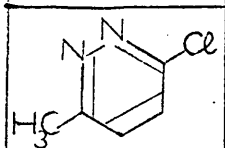
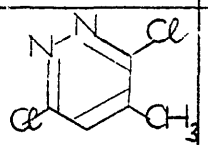
Compound in CS_2	Chemical shift in		Coupling constants in Hz.	
	Aromatics	Methyl	This work	Other work[24]
	$H_{4,5}$ 2.70(m) H_6 1.10(m)	3-CH_3 7.41	$J_{3;H_4,H_5}$ = 0 $J_{3;H_6}$ = 0.55	= 0 = 0
	H_5 2.77(m) $H_{3,6}$ 1.14(m)	4-CH_3 7.69	$J_{4;H_5}$ = 1.0 $J_{4;H_6,H_3}$ =0.65	$J_{4;H}$ = 1.0 $J_{4;H_6}$ = 0 $J_{4;H_3}$ = 0.5
	$H_{4,5}$ 2.77(s)	3,6-CH_3 7.69(s)	$J_{3,6;H_{4,5}}$ = 0	
	$H_{4,5}$ 2.72(s. sharp)	3-CH_3 7.36(s)	$J_{3;H_{4,5}}$ = 0	= 0
	H_5 2.71(quartet)	4-CH_3 7.57(d)	$J_{4;H_5}$ =0.9	=0.9

Table 1.

with the same coupling constant. The value is certainly less than the above derivative although the reason is not apparent

The above results agree well with the findings of the Japanese authors,[24] apart from the value obtained when decoupling protons H_3 and H_6 of 4-methylpyridazine (II) Table 2. However, the methyl signal of 3-methylpyridazine (IV) Table 2, previously reported to be a narrow singlet is found in our work as a rather broad signal which is quite strongly coupled. Decoupling the aromatic proton H_6 sharpens the signal considerably and very little coupling can be remaining. However decoupling of the protons H_4, H_5 produces a doublet with a separation of 0.55 Hz. This is readily reproducible and can only be explained by para coupling between the methyl group and the proton H_6. Considering the apparent lack of coupling between the methyl and the protons H_4 and H_5 this is very large indeed.

The spectrum of 3-chloro-6-methylpyridazine(V) Table 2 indicates only two signals with superposition of the aromatic protons H_4 and H_5. The halogen apparently has no effect in increasing double bond character in the 5,6 position as the methyl signal is a sharp singlet, exactly the same shape and half width as the methyl signal of 3-methylpyridazine with the aromatic proton H_6 decoupled. There is no sign of coupling of the aromatic protons with the methyl group.

On this basis it is not surprising that the methyl signal of 3,6-dimethylpyridazine (VI) Table 2 is a sharp singlet, hardly affected by decoupling the protons H_4 and H_5 and similarly the aromatic proton signal is also a sharp singlet.

These derivatives therefore exhibit splittings of the methyl signal one would expect from the interproton couplings derived from the parent compound, pyridazine. There is high double bond character in the 4,5 positions as shown with a coupling of 1.0 Hz. The apparent lack of coupling between the methyls and the aromatic protons in 3,6-dimethylpyridazine seems reasonable from the lower double bond character in the 3,4 and 5,6 positions and adds support to the idea that the small couplings in 1,4-dimethylnaphthalene and 1,4-dimethylanthracene could be due to partial localisation of the double bond in the 2,3 position, with a corresponding loss in the 1,2 and 3,4 positions.

This is also borne out in 3-methylpyridazine where there is very little coupling between the methyl and the protons H_4 and H_5. It does not explain the surprisingly large para coupling of 0.55 Hz. which is difficult to rationalise, especially if it is occurring through the same pathway i.e. via the carbons 3,4,5 and 6. There may be interaction across the ring in this case and this will be discussed in the light of results in the following chapter.

Although the magnitudes of the couplings follow the general

trend as observed in the previous sections, no account has been taken of the two nitrogensin the ring. However several heterocyclic methyl derivatives have been examined and their values are of the same order as found in this case. It does seem that ~ 1.0 Hz. is the maximum value for the coupling between a methyl group and an aromatic proton in all the aromatic hydrocarbons and heterocyclic compounds so far investigated.[6,27] A value of 1.5 Hz. for ortho side chain coupling has been recorded in acenaphthene (VII) but this large value was attributed to steric effects.[28]

One can infer a high degree of double bond character in these positions and therefore a high degree of localisation of the true double bond, despite the fact that the value of the coupling constant never reaches that of a fully localised double bond as found in propene (1.7-1.8Hz.).[4,5]

Section 4. Complex Benzylic Coupling in α-Methyl Derivatives.

Discussion

Finally, during the course of this work the asymmetric methyl signals of α-methyl substituted aromatic hydrocarbons were investigated. This asymmetry was first mentioned by Nair and Gopakumar[29] who observed that the splitting of the methyl signal of 1-methylnaphthalene was somewhat different from the normal symmetrically shaped signal. However the authors did not reproduce the methyl signal.

A few years later, Clar, McAndrew and Zander[7] also pointed out that the methyl signal of 1-methylphenanthrene was not symmetric but appeared to be a singlet with a small high field peak which they considered to be an impurity. The possibility of an impurity was very soon discounted on examination of the methyl signals of 1-methylnaphthalene (I) and 1-methylanthracene (II) which both showed the same asymmetric signal. Further investigations of 1,5-dimethylnaphthalene (III) and 1,5-dimethylanthracene (IV) showed that this asymmetric signal was a true function of the molecule. Both 1-methylanthraquinone (VI) and 1,5-dimethylanthraquinone (VII) show this effect to the same extent as their corresponding

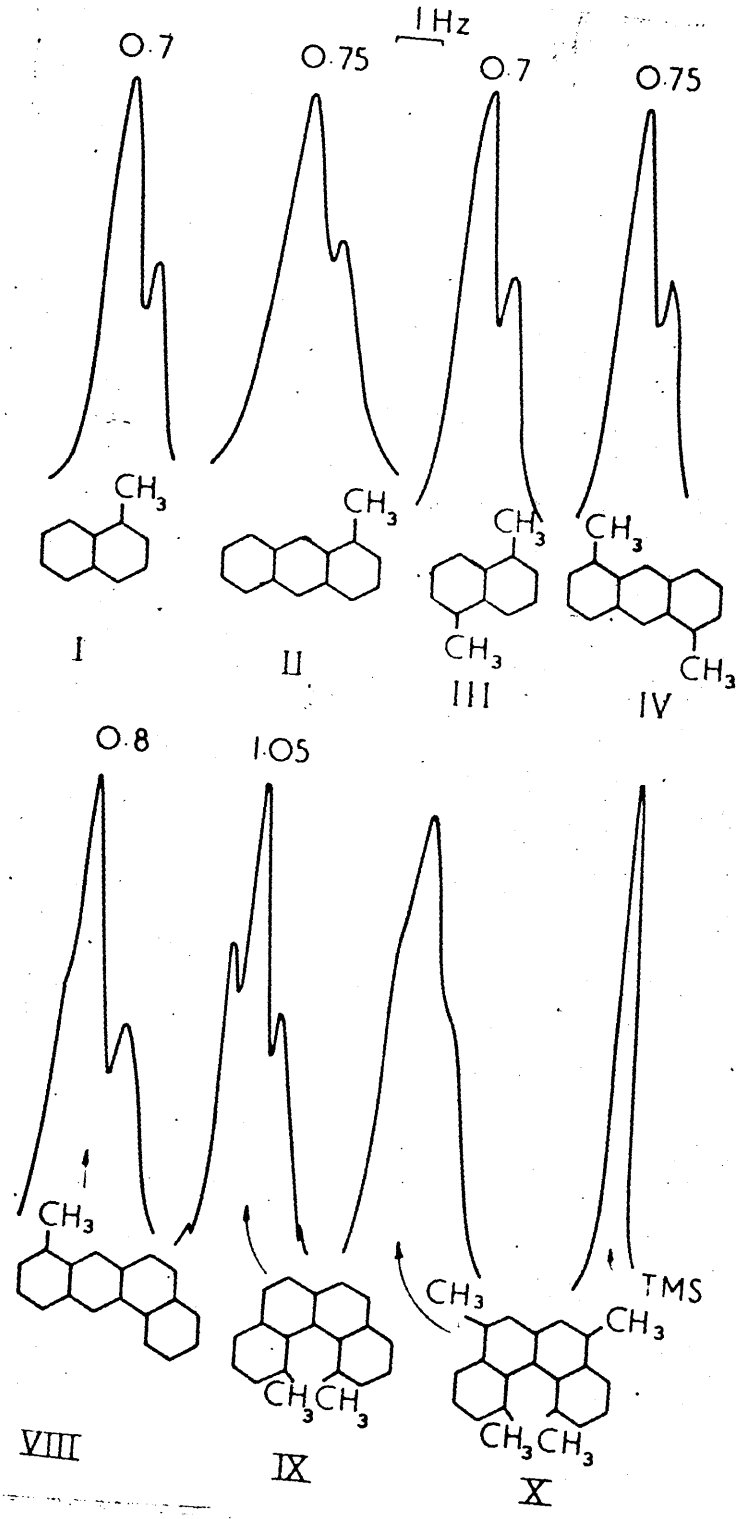


Fig 1. Comparison of the methyl signals from the N.m.r. spectra of mono- and di- α-methyl derivatives at 60 MHz.

hydrocarbons with a separation of the order of 0.7 to 0.8 Hz. and it appears to be a function of the ring to which the methyl is attached.

Decoupling of the aromatic protons indicate that the main contributions to the signal are from ortho and para couplings. It is not possible to decouple the ortho and meta protons separately, but decoupling at this frequency causes the methyl signal to form a doublet with a separation of the order of 0.5 Hz.

Decoupling at the para position does not always give a sharp doublet which may be due to the effect of the meta coupling overlying the ortho coupling, but in most cases the separation is of the order of 0.6 Hz.

To measure the effect, if any, caused by angular annellation to the system, 5-methyltetraphene (VIII) was investigated. At 60 M.Hz. the methyl signal shows this effect but appears to have a low field shoulder on the main peak, and at 100 M.Hz. the signal is a triplet. Decoupling again shows almost equal contributions from ortho and para coupling with a small unmeasurable meta coupling. This triplet signal is repeated even more clearly in 5,4'-dimethyl-3,4-benzophenanthrene (IX) and has a separation of the order of 1.0 Hz. Decoupling shows clearly couplings of the order 0.5 Hz for both ortho and para protons. However the methyl signal of 2,5,9,4'-

tetramethyl-3,4-benzophenanthrene, although a triplet, is less distinct(X).

It was tentatively assumed that this overall asymmetry of the methyl signal might be due to an additional contribution to the normal couplings via interaction between the para proton and the methyl group across the ring.

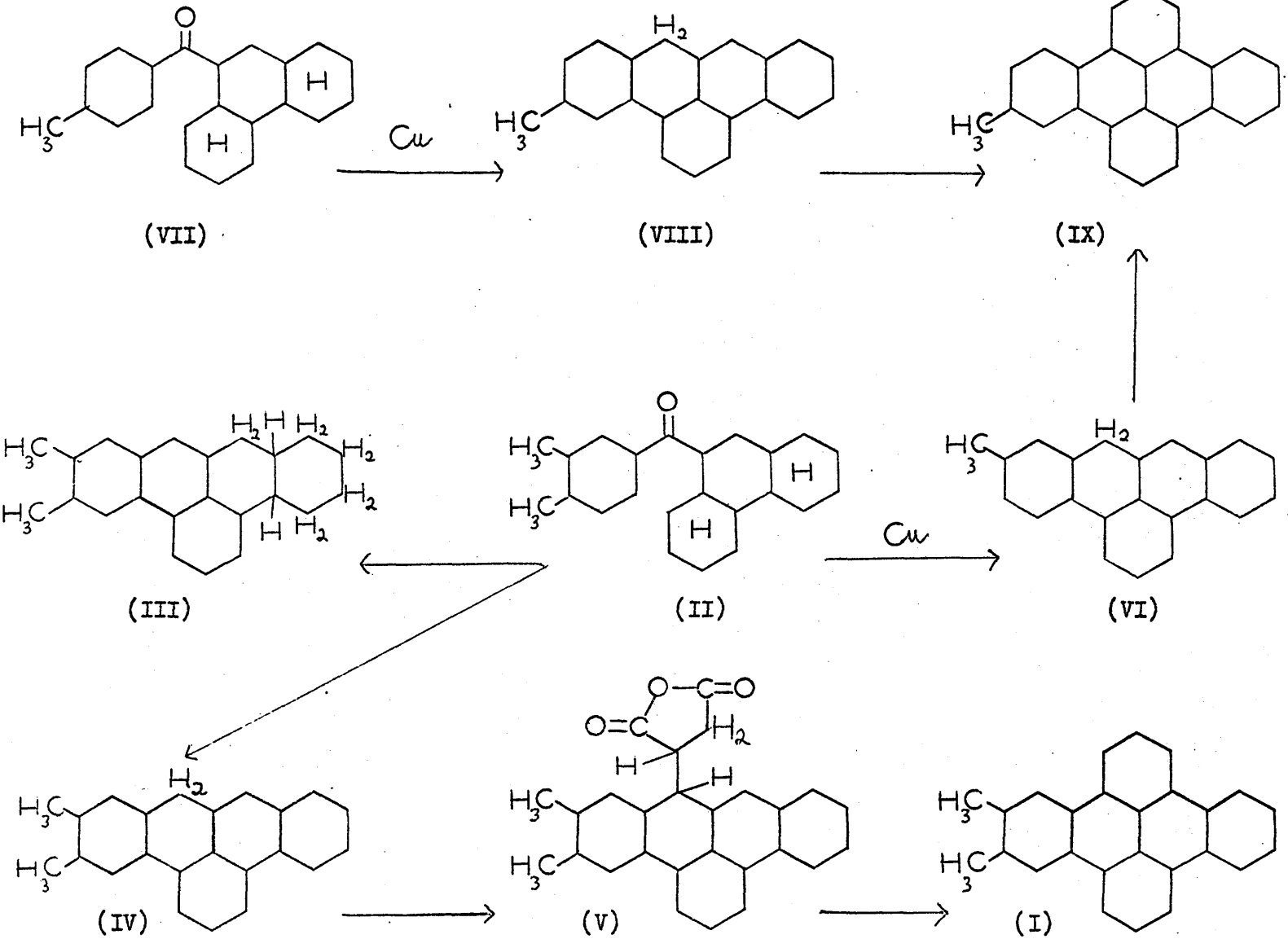
However a recent paper[30] dealing with the question of the asymmetry of the methyl signal in α-methyl substituted naphthalenes has been published. The author, using computer analysis and by varying the coupling constants, obtained a calculated signal which matches the observed methyl resonance in 1,8-dimethylnaphthalene. It therefore appears that the distorted intensities of the methyl signal are inherent when a combination of couplings of these magnitudes occurs, despite the very large chemical shift difference between the methyl protons and the aromatic protons.

However, although the author also showed that the shape of the signal is very sensitive to small changes in the order of magnitude of the couplings this did not produce a triplet signal as observed for 5-methyltetraphene and 5,4'-dimethyl-benzophenanthrene. A computer analysis of the spectra of these molecules is required before further discussion is possible, and this was not attempted in the course of this work.

Experimental Discussion

A considerable amount of the experimental work in this section dealt with repetition of literature preparations to obtain the required compounds. The compounds listed below with their relevant references are those which followed the literature description exactly: 4,5-dibromo-o-xylene[31]; 2,5-dibromo-p-xylene[32]; 2,4-dibromo-m-xylene[33]; 4-bromotoluene[34]; 2,4,5-tribromotoluene[35]; 1-bromo-4-methylnaphthalene[36]; 2-chloro-1-methylanthraquinone; 2-chloro-3-methylanthraquinone[37]; 4-methylpyridazine; 3,6-dichloro-4-methylpyridazine[38]; 3-chloro-6-methylpyridazine[39]; 3,6-dimethylpyridazine[40].

The most important part of the new synthetic work involved the synthesis and purification of 2',3'-dimethyl-1,2:6,7-dibenzopyrene (I). The method used was a modification of the synthetic scheme for the parent hydrocarbon, dibenzopyrene, which involves condensation of benzoyl chloride and octahydrophenanthrene using aluminum trichloride, and pyrolysis of the resulting ketone with copper powder at 400°.[41] The hydrocarbon, 2,3:7,8-dibenzophenalene from this process, reacts with maleic anhydride forming the succinic anhydride derivative, which on treatment with zinc chloride and sodium chloride yields the required hydrocarbon. The monomethyl derivative, 2'-methyl-1,2:6,7-dibenzopyrene (IX), is readily obtained by the above method from the ketone (VII), which is formed by condensation of p-toluyl chloride


(VII)
Cu
(VIII)
(IX)
(III)
(II)
Cu
(VI)
(IV)
(V)
(I)

and octahydrophenanthrene.

However the ketone (II), formed by condensation of 3,4-dimethylbenzoyl chloride and octahydrophenanthrene, does not give the required 2" , 3"-dimethyldibenzophenalene on pyrolysis with copper powder. Instead, a monomethyldibenzophenalene is isolated which does not have an identical n.m.r. spectrum with the previously isolated monomethyl derivative. This new compound is in fact 2"-methyldibenzophenalene (VI) formed from (II) with loss of the methyl group from the 3" position. Treatment with maleic anhydride gave the intermediate succinic acid derivative and a zinc chloride, sodium chloride melt produced the hydrocarbon 2'-methyldibenzopyrene (IX) identical with a sample from the earlier synthesis.

To prevent the loss of the methyl group, the ketone (II) was pyrolysed without copper powder thus effecting cyclisation alone. However, U.V. examination of the crude reaction mixture indicated a mixture of both the fully dehydrogenated derivative (IV) and the expected hydroderivative (III) in about equal proportions. The former hydrocarbon was obtained from the mixture after seeded crystallisation and treated with maleic anhydride in the usual manner. A zinc chloride, sodium chloride melt of the succinic acid derivative (V) furnished the crude 2',3'-dimethyl-1,2:6,7-dibenzopyrene (I). This was further purified by removing small amounts of isomeric dimethylbenzo-

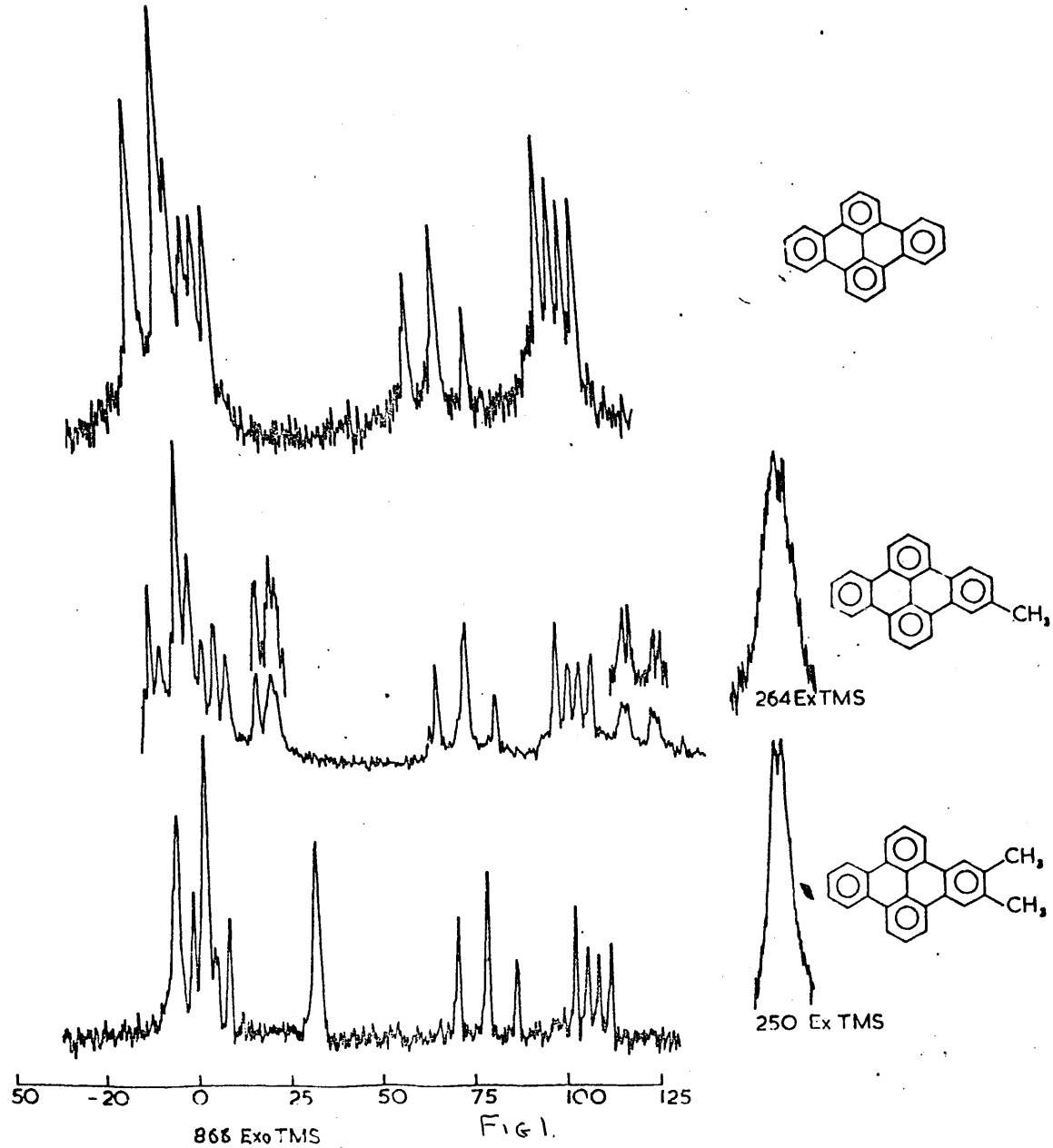


FIG 1.

N.m.r. spectra of 1,2:6,7-dibenzopyrene and the 2'-methyl and 2',3'-dimethyl derivatives at 100 MHz. Chemical shifts in Hz. exo TMS.

1,2 :6,7-Dibenzopyrene in $AsBr_3$ (corr. for CS_2); $H_{3,5,8,10}$ 759 (d) ; $H_{1',4',1'',4''}$ 858 (nα) ; $H_{4,9}$ 791 (t) ; $H_{2',3',2'',3''}$ 759 (nβ) ;

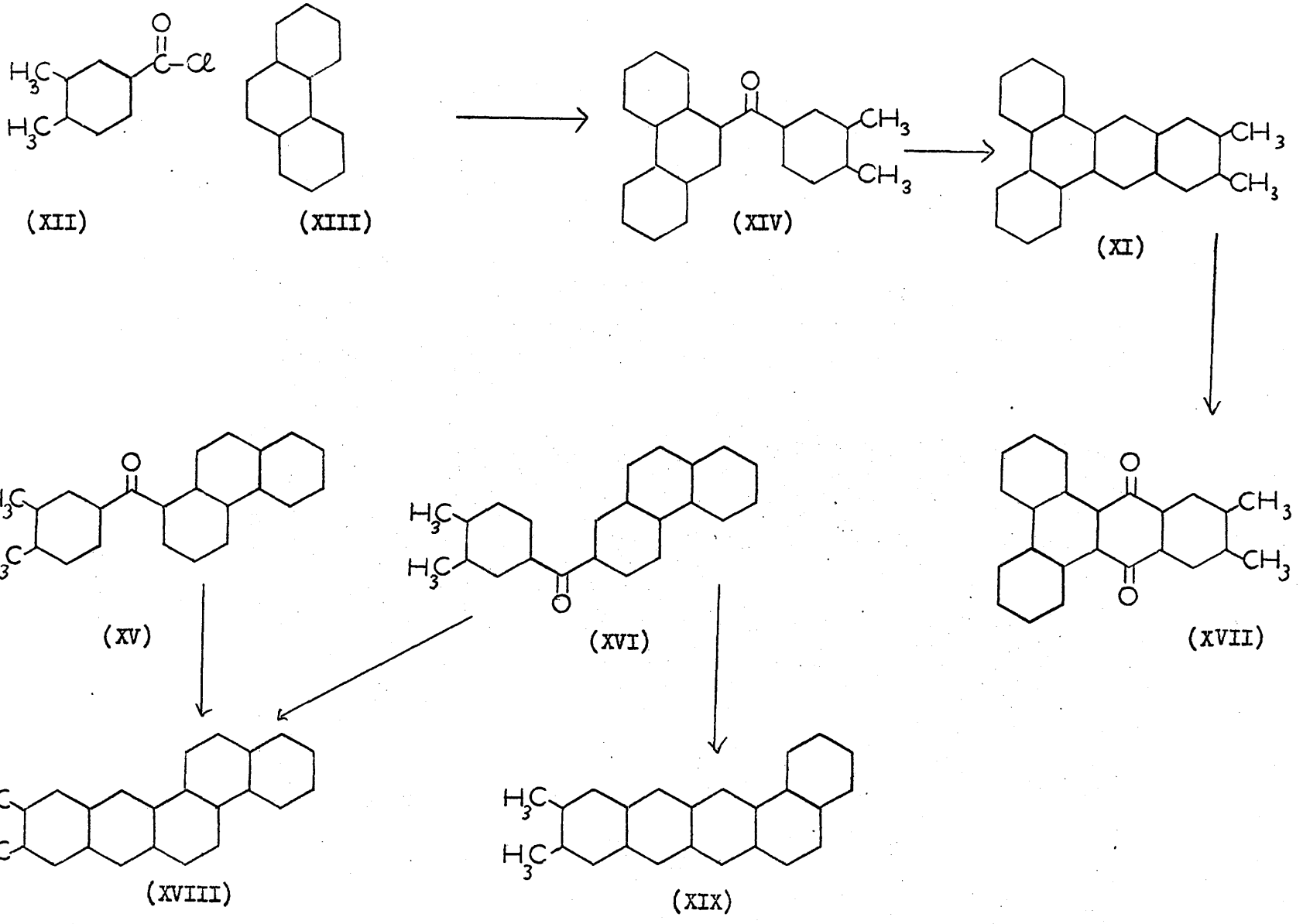
2'-Methyl- ; $H_{3,5,8,10}$ 874 (m) ; $H_{4'',1''}$ 864 (nα) ; $H_{4'}$ 850 (m) ; $H_{1'}$ 847 (m) ; $H_{4,9}$ 796 (t) ; $H_{2'',3''}$ 763 (nβ) ; $H_{3'}$ 745 (m).

2',3'-Dimethyl- ; $H_{3,5,8,10}$ 878 (d) ; $H_{1',4'}$ 858 (nα) ; $H_{1'',4''}$ 832 (s) ; $H_{4,9}$ 786 (t) ; $H_{2',3'}$ 770(nβ).

perylene (X) as its adduct with maleic anhydride, and chromatographing the hydrocarbon residue. The n.m.r. spectra of the three hydrocarbons, 1,2:6,7-dibenzopyrene and the mono and dimethyl derivatives are shown together in Fig 1 .

After refluxing the crude dimethyldibenzophenalene (IV)with maleic anhydride and extracting with dilute alkali, the hydrocarbon residue was chromatographed giving pure 1',2', 3',4',2,3-hexahydro-2",3"-dimethyl-2,3:7,8-dibenzophenalene (III) which had the U.V. spectrum of an alkylphenanthrene derivative. The n.m.r. spectrum of (III) indicates that the methyl groups, with chemical shifts 7.58 and 7.64 τ are attached to a benzene nucleus. The integration, the aromatic and aliphatic regions all support the structure (III). Therefore during cyclisation the ring with the methyl groups remains aromatic while the middle aromatic ring of the octahydrophenanthrene structure is hydrogenated. This results in the two methyl groups being permanently part of a phenanthrene complex and each signal is a singlet.

A direct comparison can be made with the methyl signals of 2",3"-dimethyl-2,3:7,8-dibenzophenalene (IV) which indicate that it consists of two isomers formed by migration of the methylene part between the positions 1 and 9. The spectrum therefore shows four sharp methyl signals, two for each isomer, which are approximately of the same intensity, and this ratio

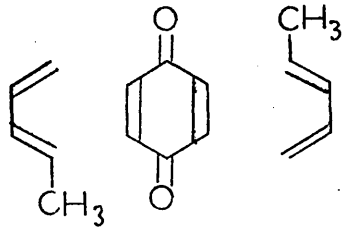

(XII)
(XIII)
(XIV)
(XI)
(XV)
(XVI)
(XVII)
(XVIII)
(XIX)

hardly alters on heating or cooling the sample. The CH_2 signal is a broad, poorly resolved multiplet . The corresponding monomethyldibenzophenalenes (VI), (VIII) each show two methyl signals exactly analogous to the dimethylderivative (IV).

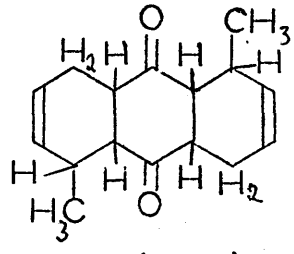
The hydrocarbon 6.7-dimethyldibenzanthracene (XI) has been synthesised as a further example of the o-dimethyl substituent effect. Condensation of 2,4,5-trimethylbenzoyl chloride (XII) with phenanthrene (XIII) gave as the main product the ketone (XIV). However smaller amounts of the isomeric ketones (XV) and(XVI) were also formed. This was shown by the pyrolysis[43] of the crude ketone mixture. The main product was the required hydrocarbon (XI). Its constitution could easily be established by the U.V. and n.m.r. spectra. Oxidation with chromic acid in acetic acid gave the quinone (XVII).

Another isomeric hydrocarbon formed by this pyrolysis was 8,9-dimethyl-3,4-benzotetraphene (XVIII) which could have originated from the ketones (XV) and (XVI). This was readily recognised from the U.V. spectrum. There was also a small amount of a yellow hydrocarbon formed from the ketone (XVI). It has the structure of 8,9-dimethyl-1,2-benzotetracene (XIX) and could be removed readily due to its high reactivity with maleic anhydride.

A literature search showed that 1,5-dimethylanthracene (XX) had been synthesised previously by Haworth and Sheldrick,[44]



(XXI) (XXII) (XXI)



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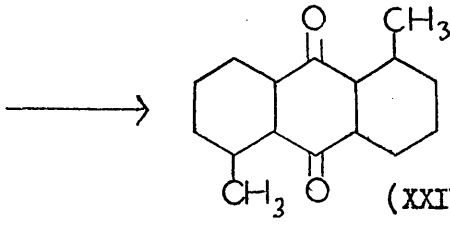

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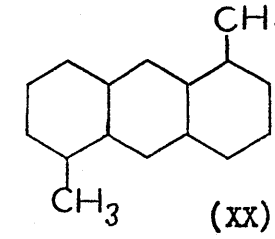

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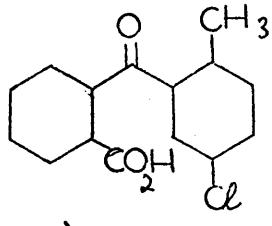

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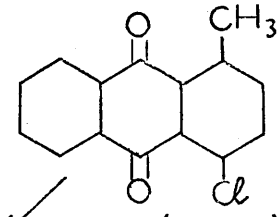

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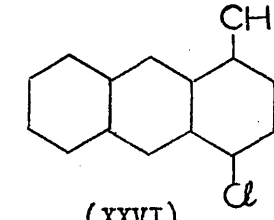

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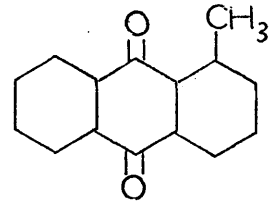

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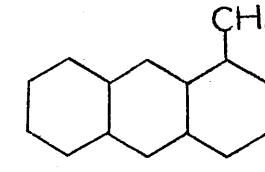

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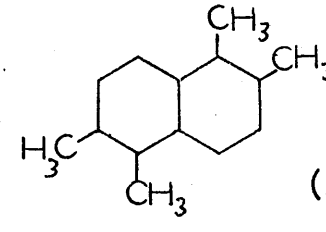

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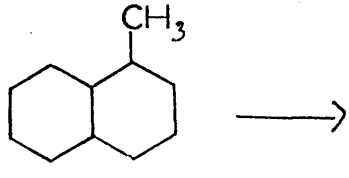

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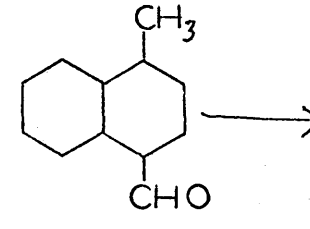

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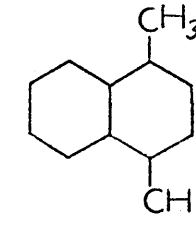


(XXXIII)

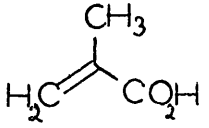
who obtained it from a by-product during the attempted synthesis of 4,5-dimethylphenanthrene. However a much simpler synthesis was carried out starting with Diels-Alder[45] addition of two molecules of 1,3-pentadiene (XXI) to benzoquinone (XXII). The resulting intermediate (XXIII) underwent enolic aromatisation with potassium hydroxide in diethylene glycol, to give 1,5-dimethylanthraquinone (XXIV). Reduction of the quinone, and purification of the reduction product via the picrate gave the required hydrocarbon (XX).

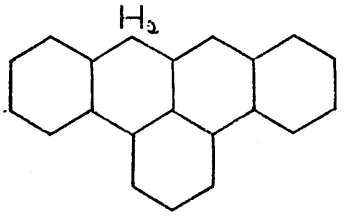
1-Methylanthracene (XXV) and 1-chloro-4-methylanthracene (XXVI) have also been synthesised previously.[46] Condensation of p-chlorotoluene with phthalic anhydride gives the keto acid (XXVII) which cyclises to the anthraquinone (XXVII) with oleum. Direct reduction of the quinone with pyridine, acetic acid and zinc dust, and chromatography of the crude product gives (XXVI).

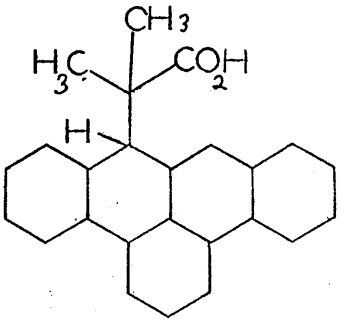
1-Chloro-4-methylanthraquinone can be dehalogenated with copper and potassium acetate in nitrobenzene[46] and the resulting 1-methylanthraquinone purified by chromatography. The hydrocarbon (XXV) is obtained by reduction of this quinone (XXIX) and purified via the picrate.

The known 1,2,5,6-tetramethylnaphthalene (XXX) was formed by addition of dimethyl sulphate to the intermediate product from n-butyllithium[47] and 1,5-dibromo-2,6-dimethylnaphthalene and was purified by chromatography. The bromination of 2,6-

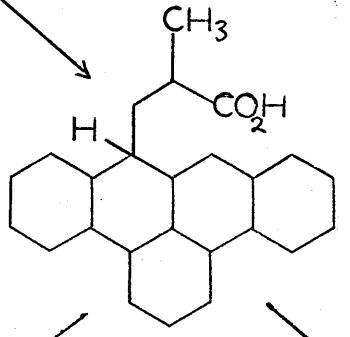
(XXXV)



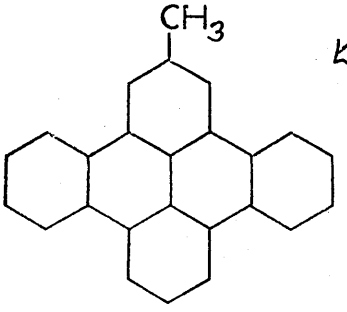




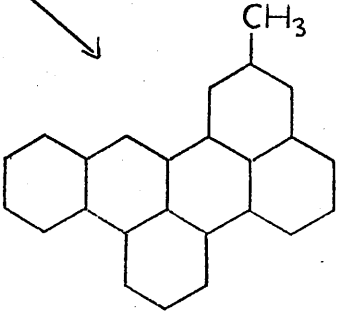
(XXXVIa)



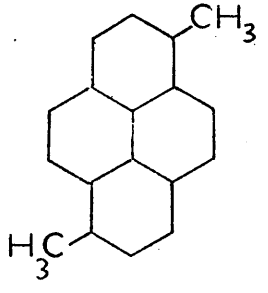
(XXXVI)



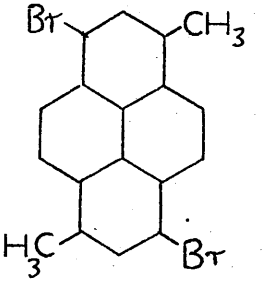
(XXXIV)



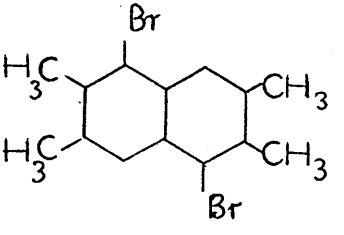
(XXXVII)



(XXXVIII)



(XXXIX)



(XL)

dimethylnaphthalene gave improved yields over the literature preparation.[48] A Reiche aldehyde substitution on 1-methylnaphthalene (XXXI) gave the known 1-formyl-4-methylnaphthalene[49] (XXII) exclusively. Reduction with hydrazine hydrate and distillation gave the pure product, the known 1,4-dimethylnaphthalene (XXXIII).

The triplet methyl signal observed in the n.m.r. spectra of both 4-methyl and 4,9-dimethylpyrene prompted the synthesis of 4-methyldibenzopyrene (XXXIV) in order to see if this effect was repeated. Methylacrylic acid (XXXV) reacts with 2,3:7,8-dibenzophenalene in a similar manner to maleic anhydride forming the intermediate acid (XXXVI). The n.m.r. spectrum of this product showed that although both possible isomers (XXXVI) and (XXXVIa) had been formed, unfortunately (XXXVIa) was by far favoured over the required isomer. However a zinc chloride, sodium chloride melt of the crude acid mixture did yield a small amount of the required hydrocarbon (XXXIV) but after purification from the isomeric methylbenzoperylene (XXXVII) only enough product to allow an analysis, U.V. spectrum and mass spectrum was available.

The lack of coupling between the methyl group and the protons ortho and meta to it in 3-methylpyrene and 3.8-dimethylpyrene (XXXVIII) has been discussed. In order to see if a bromine substituent in the meta position would enhance the coupling

between the methyl group and the remaining ortho proton, 3,8-dibromo-5,10-dimethylpyrene (XXXIX) was obtained free of isomers by direct bromination of the hydrocarbon (XXXVIII), in carbon disulphide. In particular, 1,5-dibromo-2,3,6,7-tetramethylnaphthalene (XL) and 1-bromo-2,3-dimethylnaphthalene (IVa), and in general, the simpler bromo derivatives discussed in this work were formed by this method of bromination, and purified by crystallisation or vacuum distillation.

EXPERIMENTAL

3,4-Dimethylacetophenone

Prepared by Friedel-Crafts reaction of acetyl chloride and o-xylene using aluminium trichloride. The product was purified by vacuum distillation Bpt. 135-138° (20 m.m.) (Lit . B.pt. 246-7°).[50]

3,4-Dimethylbenzoic acid

The above acetylxylene (300 gm.) was slowly added to a stirred solution of 4½ litres of commercial sodium hypochlorite (10%) at 80°. The addition was exothermic and the temperature rose and was maintained at 100° for 40 minutes, until the organic layer had almost completely reacted and the aqueous layer was pale yellow. The mixture was cooled, extracted with ether to remove unreacted ketone and excess hypochlorite destroyed with sodium metabisulphite powder. The resulting solution was acidified with concentrated hydrochloric acid yielding the acid as a white precipitate which was washed with water and dried. Yield 228 gm. m.pt. 162-164°. (Lit. m.pt. 166°).[51]

3,4-Dimethylbenzoyl Chloride

This was prepared exactly as described by Morgan and Coulson by refluxing the acid with excess thionyl chloride. Vacuum distillation gave the pure acid chloride (210 gm.) B.pt. 150-155° (25 m.m.). (Lit. B.pt. 188° (140 m.m.)).[52]

9-xyloyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (II)

The acid chloride (210 gm.) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (220 gm.) were dissolved together in 900 mls. of dry benzene. Finely powdered aluminium chloride (250 gm.) was added in three portions with stirring. The solution was orange red initially, becoming dark reddish-brown after addition of all the aluminium chloride. The mixture was stirred for two hours at room temperature until no more hydrogen chloride gas was evolved. The dark red viscous melt was decomposed with ice and dilute hydrochloric acid, and the oily organic layer separated from the aqueous layer, washed with dilute ammonia and water and dried with anhydrous sodium sulphate. The solvent was removed by distillation leaving the crude ketone (372 gm.) as a thick reddish brown oil. A sample of the ketone was triturated with ether affording a white crystalline product which on further recrystallisation from alcohol gave short colourless prisms m.pt. 107-109° and gave a yellow solution with concentrated sulphuric acid.

Found	C=86.40%, H=8.20%
$C_{23}H_{26}O$ requires	C=86.75%, H=8.23%

2",3"-Dimethyl-2,3:7,8-dibenzophenalene (IV).

The above crude ketone (370 gm.) was heated to 390-400° in a distillation apparatus. The liquid darkened much less than during other Elbs reactions. After 30 mins. no more water was evolved and the amount of water in the receiver flask measured 19 mls., almost the theoretical volume. The residue in the flask was a light brown glass which crystallised when triturated with light petrol (100-120°). The resulting precipitate (40 gm.) was filtered and washed with light petrol. Chromatography of a sample with light petrol (60-80°) and benzene on Grade I neutral alumina gave a solution with a blue fluorescence. Concentration yielded colourless needles m.pt. 148-150° which dissolved in concentrated sulphuric acid with a deep red colour and an orange fluorescence. The U.V. spectrum is shown in Fig. 2.

Found	C=93.63%, H=6.29%
$C_{23}H_{18}$ requires.	C=93.84%, H=6.16%

2",3"-Dimethyl-2,3:7,8-dibenzophenalyl-9-succinic anhydride (V).

The above hydrocarbon (10 gm.) and maleic anhydride (10 gm) were refluxed in 75 ml. of dry xylene under carbon dioxide for five hours. On cooling a portion of light brown crystalline product precipitated, this was filtered and retained (2 gm.).

The xylene solution was steam distilled and the resulting pale yellow-orange organic residue was dissolved in dilute aqueous sodium hydroxide. The solution was quickly gravity filtered and acidified hot with concentrated hydrochloric acid. The resulting gum, on boiling with excess concentrated hydrochloric acid, yielded a pale cream precipitate which was filtered, washed with water and dried (11 gm). Recrystallisation from benzene yielded colourless prisms m.pt. 213-214° which gave a deep magenta solution with concentrated sulphuric acid.

Found C=79.16%, H=5.48%

$C_{27}H_{22}O_4$ requires C=79.01%, H=5.40%

The anhydride was not obtained in a pure state for analysis.

1'.2'.3'.4'.2.3-Hexahydro-2".3"-dimethyl-2,3:7.8-dibenzophenalene(III)

After dissolving the above acid derivative in dilute alkali and filtering the solution, an orange residue (0.14 gm.) remained whose U.V. spectrum was that of a substituted phenanthrene. This product was dissolved in xylene, the solution filtered, dried and concentrated. Chromatography over Grade I neutral alumina, eluting with light petrol (40-60°) and benzene gave a colourless solution with a blue fluorescence. Concentration of this solution gave colourless crystals (70 mgs.). Recrystallisation from light petrol (100-120°) yielded colourless

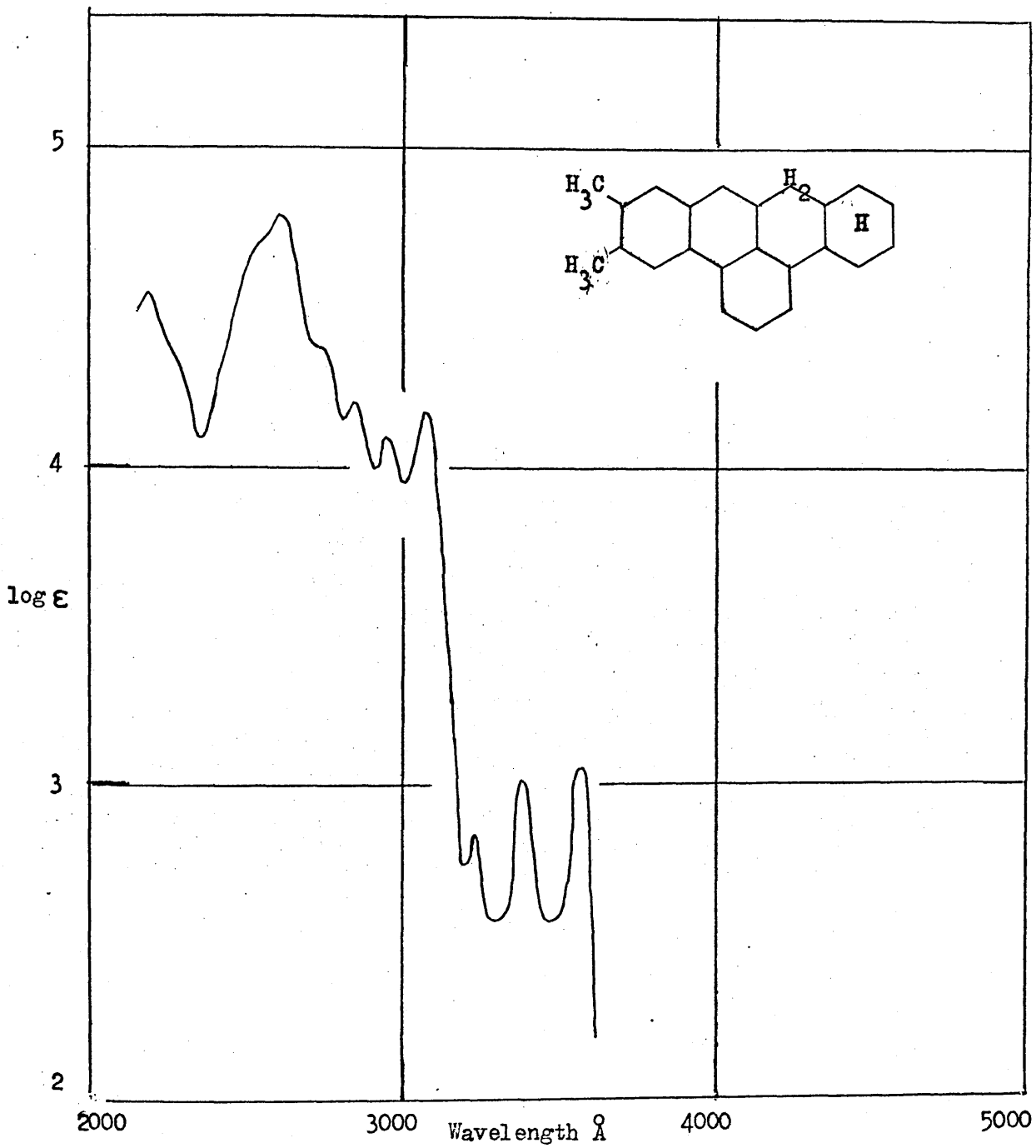


Fig.1 Absorption max. (Å) and logε (in parentheses) 1',2',3',4',2,3- Hexahyrdo-2",3"-dimethyl-2,3:7,8-dibenzophenalene in cyclohexane α :3570(3.04),3390(3.00),3220(2.83); ρ : 3070(4.24),2950(4.10), 2840(4.20),2750(4.37); β :2610(4.79); β′ :2180(4.52).

prisms m.pt. 169-171° which gave no colour with concentrated sulphuric acid. The U.V. spectrum is shown Fig. 1. The n.m.r. spectrum in CS_2 at 60 M.Hz. τ : 1.7(2H) multiplet; 2.6(4H) multiplet; 7.58 (3H) singlet; 7.62 (3H) singlet; 8.4 (9H) broad multiplet.

Found	C=92.03%,	H=8.02%
$C_{23}H_{24}$ requires	C=91.95%,	H=8.05%

2',3'-Dimethyl-1.2:6.7-dibenzopyrene (I).

The above acid (5 gm.) , fused zinc chloride (35 gm.) and sodium chloride (8 gm.) were powdered together and the mixture heated to 310° for 10 minutes. The melt separated into two layers, a wine red organic layer floating on the colourless inorganic mixture. The melt was cooled, powdered and thoroughly extracted with boiling xylene. The dark brown solution was filtered, dried and concentrated. The solution was chromatographed over Grade I neutral alumina eluting with hot xylene, gave firstly dimethyldibenzophenalene and then dimethyldibenzopyrene which according to U.V. spectral examination also contained some of the isomeric dimethylbenzoperylene. Concentration gave a mixture of these two hydrocarbons (0.7 gm.) which was refluxed with excess maleic anhydride and crystal of iodine in order to remove the perylene derivative. The melt was poured

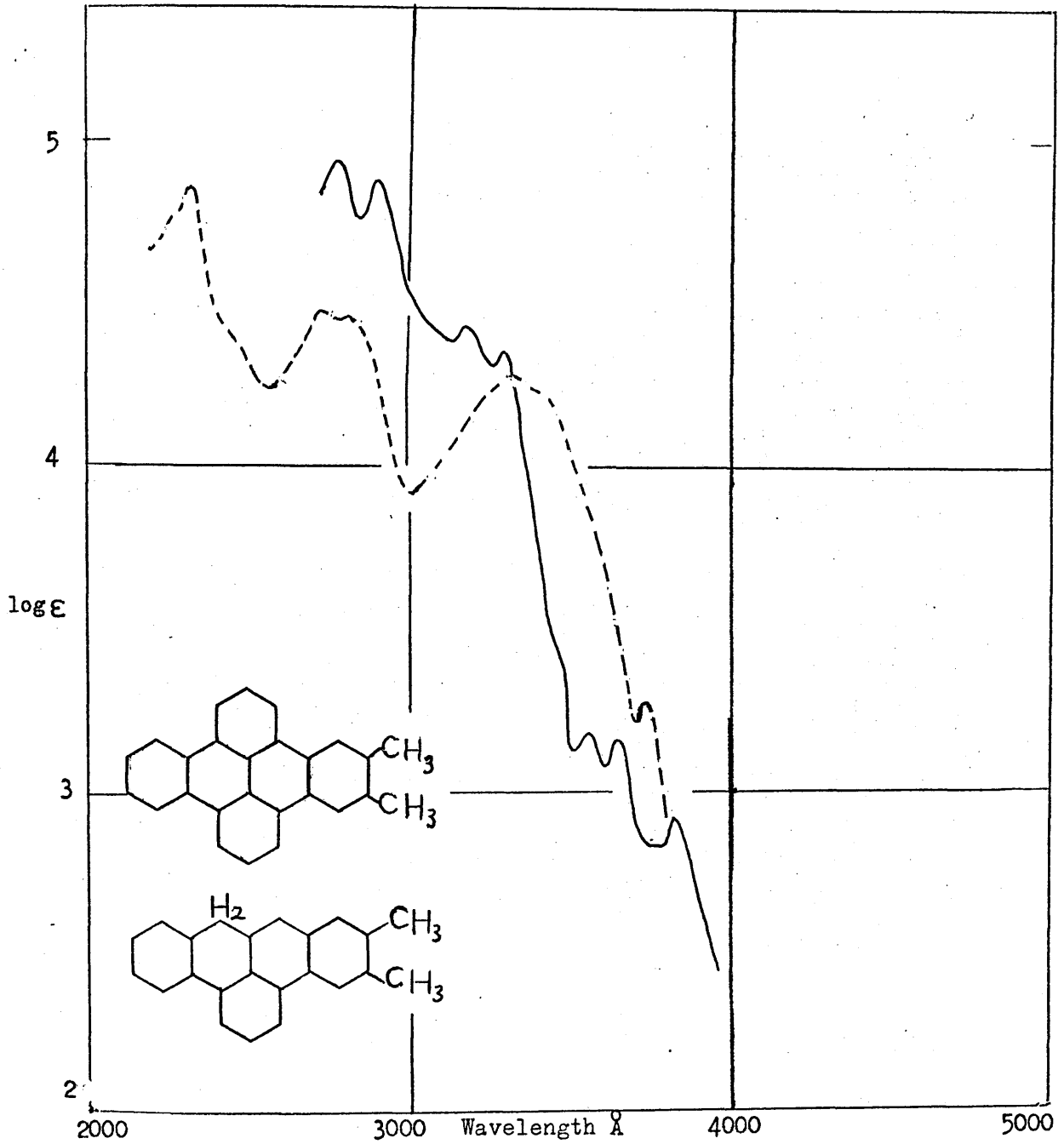


Fig. 2 Absorption max. (Å) and log ε (in parentheses)
---------- 2',3' - Dibenzo-2,3:7,8-pyrene in benzene α : 3840(2.91), 3660(3.15), 3570(3.17); ρ : 3310(4.36), 3180(4.43); β : 2920(4.88), 2790(4.94).
- - - - - 2",3"-Dimethyl-2,3:7,8-dibenzophenalene in cyclohexane
α : 3740(3.24); ρ : 3400(4.20), 3320(4.25); β : 2780(4.45), 2730(4.50); β′ : 2300(4.84)

into water and extracted with dilute sodium hydroxide to remove the acidic condensation product of the perylene derivative and maleic anhydride. The residue (0.4 g.) was filtered off and dissolved in xylene. The dried, concentrated solution was chromatographed over a short column of alumina and concentration of the xylene eluant gave almost colourless needles, m.pt. 249-250° which did not dissolve in concentrated sulphuric acid. The U.V. spectrum in shown in Fig. 2.

Found	C=94.79%,	H=5.35%
$C_{26}H_{18}$ requires	C=94.51%,	H=5.49%

2,4,5-Trimethylacetophenone

This was prepared by Friedel-Crafts reaction of acetyl chloride and pseudo-cumene using aluminium chloride, and purified by vacuum distillation. B.pt. 140° (25 m m.) (Lit. 137-138°(20m.m.)[53]

2,4,5-Trimethylbenzoic acid.

Exactly as described for the sodium hypochlorite oxidation of 3,4-dimethylacetophenone. Yield 110 gm. from 150 gm. of ketone. m.pt. 144-148° (Lit. m.pt. 150°).[54]

2,4,5-Trimethylbenzoyl chloride.

This was prepared by refluxing the above acid with excess thionyl chloride and vacuum distilling the product, yield 80 gm. B.pt. 180-185° (25 m.m.).

9-(2,4,5-trimethylbenzoyl)-phenanthrene (XIV)

The acid chloride (75 gm.) and phenanthrene (66 gm.) were dissolved in benzene (100ml.). Powdered aluminium chloride (75 gm.) was added in two portions with stirring. The mixture was orange red initially becoming darker after additon of all the aluminium chloride. After the evolution of hydrogen chloride ceased, the melt was decomposed with ice and dil. hydrochloric acid. Xylene was added, and the organic layer washed with hot water and dilute ammonia. In order to remove moisture, some of the solvent was distilled off, and the solution filtered. On standing overnight crystals (19 gm.) separated. Recrystallisation from ethanol yielded long pale yellow prisms, m.pt. 192 -194° which dissolved in concentrated sulphuric acid forming a yellow solution.

Found	C=88.34%,	H=6.43%
$C_{24}H_{20}O$ requires	C=88.85%,	H=6.21%

6.7-Dimethyl-1,2:3.4-dibenzanthracene (XI)

The above xylene solution of the ketones was boiled to remove the solvents. After further heating at 420° for 30 minutes the evolution of water ceased. On cooling the dark brown glass was dissolved in xylene, traces of water removed by boiling, and the concentrated solution chromatographed over Grade I neutral

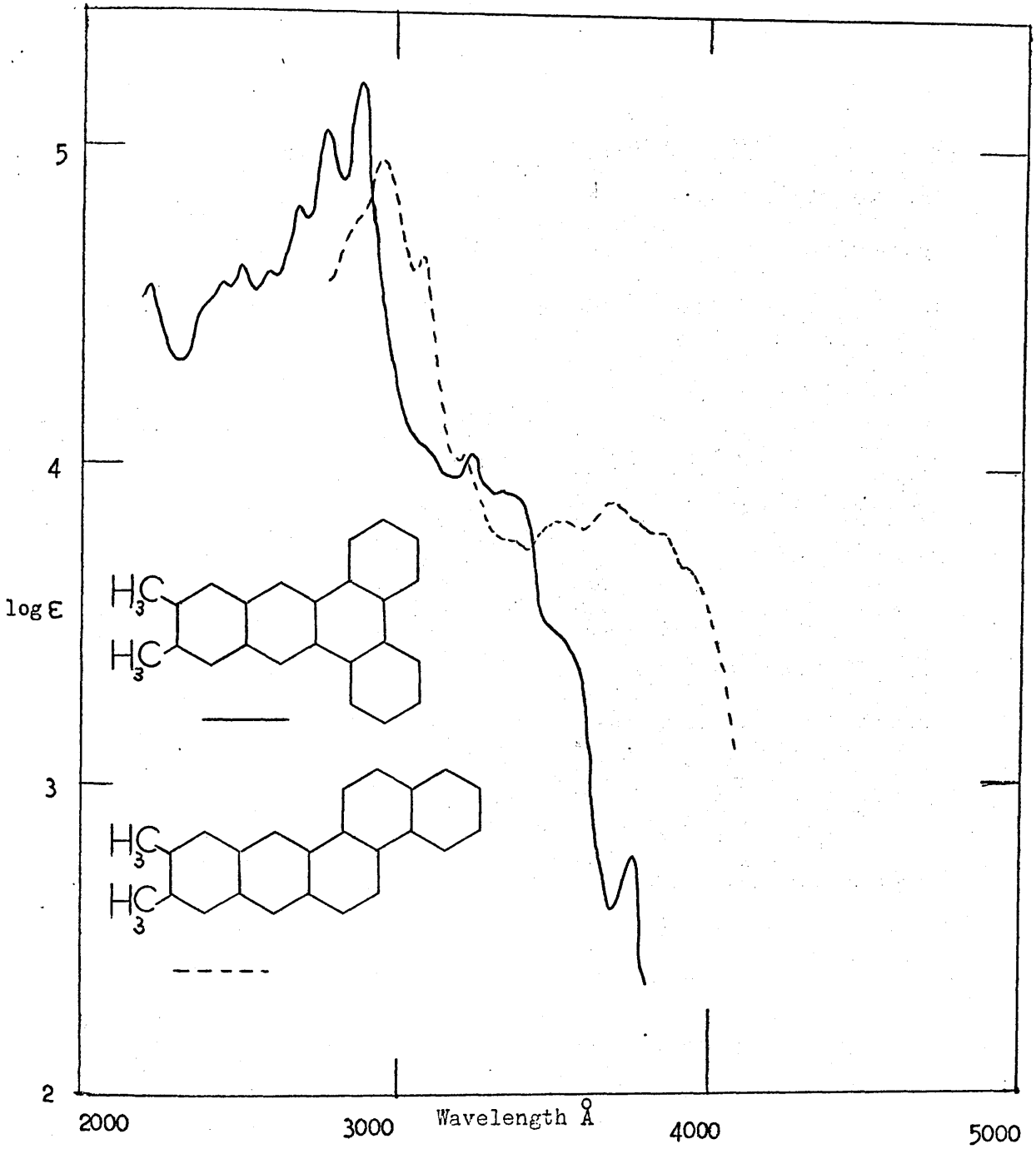


Fig.3 Absorption max. (Å) and log ε (in parentheses)

——— 6,7-Dimethyl-1,2:3,4-dibenzanthracene in cyclohexane α :3780(2.79); ρ: 3490(3.51),3350(3.92),3220(4.01); β : 2890(5.19),2785(5.04),2680(4.79), 2500(4.62).

----- 9,10-Dimethyl-3,4-benzotetraphene in benzene α :3950(3.65); ρ:3860(3.79) 3680(3.88),3510(3.82),3120(4.02); β :3080(4.65),2940(4.94),2860(4.75).

alumina. Eluting with xylene gave firstly a colourless solution with a blue fluorescence which showed the U.V. spectrum of a 1,2:3,4-dibenzanthracene derivative. All the following fractions showing this spectrum were united and concentrated. Pale yellow leaflets were obtained which after further recrystallisation from xylene had m.pt. 219-220° and dissolved in concentrated sulphuric acid to give a blue-green solution. The U.V. spectrum is shown in Fig. 3.

Found		C=93.96%,	H=6.04%
$C_{24}H_{18}$	requires	C=94.08%,	H=5.92%

9,10-Dimethyl-3,4-benzotetraphene (XVIII)

The latter fractions from the column showing the U.V. spectrum of a 3,4 - benzotetraphene derivative were united. Concentration yielded bright yellow crystals (3 gm.). The U.V. spectrum indicated that they contained the isomer, 8,9-dimethyl-1.2-benzotetracene with ρ-bands at 4540 and 4250Å. This could be removed by treating a dilute boiling xylene solution of the hydrocarbon mixture (1.3 gm.) with small amounts of maleic anhydride until these bands disappeared from the spectrum. On cooling pale yellow plates crystallised and after recrystallisation from xylene gave m.pt. 308-309°, dissolving in concentrated sulphuric acid with a magenta solution. The U.V. spectrum

is shown in Fig. 3.

Found C=93.79%, H=6.01%

$C_{24}H_{18}$ requires C=94.08%, H=5.92%

6,7-Dimethyl-1.2:3.4-dibenzanthraquinone (XVII)

6,7-Dimethyl-1.2:3.4-dibenzanthracene (0.5 gm.) was suspended in acetic acid (10 ml.) and refluxed with a slight excess of chromium trioxide (0.2 gm.) for 30 minutes. The purple solution rapidly became green. Water was added and the precipitate filtered off, washed with water and dried. (0.4 gm.). Recrystallisation twice from ethanol yielded small thin orange-yellow needles m.pt. 237-238° which dissolved in concentrated sulphuric acid to give an emerald green colour. The U.V. spectrum in ethanol; λ_{max} 4030(3.76); 3050(4.40); 2885(4.57); 2690(4.69); 2480 (4.78).

Found C=85.52%, H=4.89%

$C_{24}H_{16}O_2$ requires C=85.69%, H=4.79%

2,3:7,8-Dibenzophenalene.

This was prepared by pyrolysis with copper powder at 400° C of the product obtained from the Friedel-Crafts condensation of octahydrophenanthrene, benzoyl chloride and aluminuim chloride. After pyrolysis the pure dibenzophenalene was obtained by vacuum distillation as a pale yellow solid.

2,3:7,8-dibenzophenalyl-γ-isopropylic acid (XXXVI).

Dibenzophenalene (6 gm.) was refluxed with methylacrylic acid (15 gms.) for 1½ hours at 120°. The resulting mixture was diluted with water and thoroughly extracted with dilute ethanolic sodium hydroxide solution. The pale yellow extract was filtered, boiled to remove the ethanol and acidified hot with concentrated hydrochloric acid. The resulting yellow precipitate was filtered, washed with water and dried (3 gm.). A sample was recrystallised from xylene giving off-white nodules m.pt. 223-224°, which gave a cherry red solution in concentrated sulphuric acid.

Found	C=84.83%, H=6.05%
$C_{24}H_{20}O_2$ requires	C=84.71%, H=5.88%

4-Methyl-1,2:6,7-dibenzopyrene. (XXXIV)

The above acid (5 gm.) was thoroughly powdered with zinc dust (5 gm.) and sodium chloride (12.5g). Fused zinc chloride (25 g.) was added and the mixture was heated with stirring at 310° for 10 minutes. The product was allowed to cool to 100°, dil. acetic acid was added and the mixture boiled for a few minutes. The product was filtered, powdered and boiled with concentrated hydrochloric acid to destroy excess zinc. The remaining light brown solid was filtered, washed with dil. ammonia,

water and dried. The solid product was thoroughly extracted with xylene giving a dark brown solution with a green fluorescence. The dried, concentrated xylene solution was chromatographed over Grade I neutral alumina. The initial eluate with benzene proved to be mainly dibenzophenalene. The latter fractions, eluting with xylene, on U.V. examination proved to contain the required compound. Concentration of these fractions yielded 12 mg. of a yellow non-uniform crystalline powder. To remove the main impurity, methylbenzoperylene, the benzene solution was shaken for a few minutes with concentrated sulphuric acid. The acid layer became purplish-red as the benzoperylene derivative dissolved in the acid. The almost colourless organic layer was thoroughly washed with dil. ammonia and water and dried over anhydrous sodium sulphate. Concentration of the solution yielded tiny yellow needles (4 mg.) m.pt. 267-271° which did not dissolve in concentrated sulphuric acid. M.S. molecular ion $^{m}/_{e}$=316; calculated M.W. = 316. U.V. spectrum in cyclohexane, λ max. α : 3860(2.75), 3740(2.80); ρ : 3280(4.24), 3150(4.36); β : 2875(4.72), 2760(4.78); β' : 2250(4.91).

Found		C=94.51%, H=5.21%.
$C_{25}H_{16}$	requires	C=94.94%, H=5.06%

1,5-Dibromo-2,3,6,7-tetramethylnaphthalene (XL)

2,3,6,7-Tetramethylnaphthalene (0.25 gm.) was dissolved in carbon disulphide (5ml.) and a slight excess of bromine (0.6gm.) in carbon disulphide was added slowly with the exclusion of light. A crystal of iodine was added and the mixture left overnight. The solvent was removed and the residue dissolved in benzene and filtered. Several recrystallisations of the precipitate from the benzene solution, using light petrol (60-80°) gave colourless leaflets m.pt. 216-217° which did not dissolve in concentrated sulphuric acid. The n.m.r. spectrum indicated that the recrystallised product was free of the isomeric 1,4-dibromo derivative which was present in the crude reaction product.

Found		C=49.32%, H=4.17%
$C_{14}H_{14}Br_2$	requires	C=49.12%, H=4.09%

3,8-Dibromo-5,10-dimethylpyrene (XXXIX)

3,8-Dimethylpyrene (40 mgs.) was dissolved in carbon disulphide (3 ml.) and a slight excess of bromine (60 mgs.) in carbon disulphide (1 ml.) was added dropwise. After standing overnight with a crystal of iodine, the solvent was distilled and repeated recrystallisation from xylene gave pale yellow needles m.pt. 284-286° which did not dissolve in concentrated sulphuric acid.

Found C=55.39%, H=3.27%

$C_{18}H_{12}Br_2$ requires C=55.67%, H=3.08%

1,5-Dibromo-2,6-dimethylnaphthalene

2,6-Dimethylnaphthalene (50 gm.) was dissolved in carbon disulphide (125 gm.) and bromine (120 gms.) added dropwise under exclusion of light. After gently refluxing for 40 hours, no futher hydrogen bromide was evolved and the solvent was distilled off. The mainly solid product was filtered and washed with light petrol (40-60°) to remove a small amount of oily monobromo derivative Two recrystallisations from light petrol (100-120°) gave long flat colourless prisms (32 gm.) m.pt. 160° (Lit. m.pt. 160-161°)[48].

1,2,5,6-Tetramethylnaphthalene (XXX)

Lithium (9gm.) was dissolved in an ethereal solution of n-butylbromide (85 gm.) under nitrogen. 1,5-Dibromo-2,6-dimethylnaphthalene (10 gm.) in benzene was added dropwise and the dark red solution became pale and cloudy. The solution was refluxed for two hours. Dimethyl sulphate (130 gm .) was added dropwise to the cooled solution giving a very vigorous reaction. The mixture was refluxed for a further hour and decomposed with 5% sulphuric acid. The organic layer was dried with anhydrous sodium sulphate, reduced to small volume and chromatographed over Grade I neutral alumina. The eluate with light petrol (60-80°) yielded, on concentration, colourless

prismatic crystals (4.4 g.), which gave elongated prisms on recrystallisation from ethanol m.pt. 115-116° (Lit. m.pt. 116°), dissolving in concentrated sulphuric acid with a leaf green colouration.

Found		C=91.48%, H=8.77%
$C_{14}H_{16}$	requires	C=91.31%, H=8.70%

1,5-Dimethyl-1,4,5,8-tetrahydroanthraquinone (XXIII)

Recrystallised benzoquinone (8 gm.), 1,3-pentadiene (20 ml.) and dry xylene (10 ml.) were heated together in a sealed tube at 150° for 8 hours. The light brown viscous solution from four such tubes was then heated under vacuum to remove the solvent and excess pentadiene. The resulting gum was refluxed with alcoholic potassium hydroxide solution for 15 mins. giving a thick matt of crystals and some rubber-like resin. The crystals were filtered, washed with a little alcohol and water and dried. Yield = 20 gm. A portion was recrystallised from acetic acid giving long thin colourless needles, 190-210°(sublimes) which did not dissolve in concentrated sulphuric acid.

Found		C=78.47%, H=8.27%
$C_{16}H_{20}O_2$	requires	C=78.65%, H=8.25%

1,5-Dimethylanthraquinone (XXIV).

Crude 1,5-dimethyl-1,4,5,8-tetrahydroanthraquinone (5 gm.) was dissolved in boiling diethylene glycol (20 ml.) giving a pale yellow solution. Potassium hydroxide pellets (10 gm.) were added and the solution became dark green-brown. The mixture was refluxed for 20 mins. and on cooling yielded yellow brown needles which were filtered, washed and dried. (3 gm.) Recrystallisation from xylene gave long bright yellow needles m.pt. 188-189° (Lit. m.pt. 190°)[44] which dissolve in concentrated sulphuric acid forming an orange solution.

Found		C=81.46%, H=5.28%
$C_{16}H_{12}O_2$	requires	C=81.39%, H=5.08%

1,5-Dimethylanthracene (XX).

An intimate mixture of 1,5-dimethylanthraquinone (500 mg.) finely powdered zinc dust (5 gm.) and a few drops of water were heated together in a sealed tube at 250°. The contents of the tube were powdered and extracted with xylene. The xylene solution was dried, concentrated and chromatographed over Grade I neutral alumina eluting with light petrol (60-80°). The fractions were bulked and concentrated (105 mg.), but repeated recrystallisation from ethanol did not give a satisfactory analysis and the n.m.r. spectrum indicated the presence of the dihydro

compound. The crude anthracene was dissolved in a few ml. of ethanol and the hot solution added to a warm solution of picric acid in ethanol. The resulting picrate was recrystallised from ethanol yielding bright crimson needles m.pt. 166-167° (Lit. m.pt. 168-169°).[44]

Found C=60.87%, H=4.04%, N=9.68%.

$C_{22}H_{17}N_3O_7$ requires C=60.70%, H=3.90%, N=9.65%.

Decompositon of the picrate.

A solution of the picrate (60 mgs.) in xylene was shaken with dil. ammonia. The organic layer was washed with water, dried and the solvent evaporated. Recrystallisation from ethanol gave beautiful pale yellow layered platelets m.pt. 135-137° (Lit. m.pt. 139-140°)[44] which dissolved in concentrated sulphuric acid forming an olive green solution which darkened on standing.

Found C=93.01%, H=6.96%.

$C_{16}H_{14}$ requires C=93.16%, H=6.84%.

CHAPTER 2.

PARA and LONG RANGE COUPLINGS in METHYL and HALOGEN DERIVATIVES of LINEAR ACENES and OTHER HYDROCARBONS.

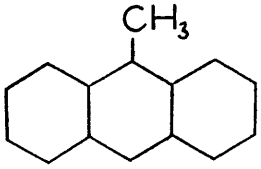
INTRODUCTION

Long-range coupling in aromatic and conjugated systems has been increasingly investigated[1,4] in recent years as better resolution of proton resonance signals is now possible. In general these couplings are small and difficult to detect, especially in aromatic hydrocarbons. However, recently a computer analysis of the naphthalene spectrum indicates that even inter-ring couplings are as high as 0.8 Hz.[5]

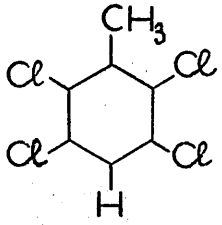
In this work we have found that a methyl substituent on a non-terminal ring of anthracene or tetracene eg. 9-methyl-anthracene shows a high degree of coupling only with the para proton, H_{10} on the same ring. The methyl resonance is a doublet and is sharpened to a singlet only by decoupling the para proton.

On the other hand, in the corresponding hydrocarbons, decoupling experiments indicate that there is no para coupling between protons on the same non-terminal ring, for example protons H_9 and H_{10} of 1-chloroanthracene. However decoupling does show that there is considerable trans-peri coupling between the peri protons of a terminal ring and those on the adjacent ring in suitably halogenated anthracenes and tetracenes. There is no evidence of either para or peri coupling between the protons on the non-terminal rings of tetracene derivatives.

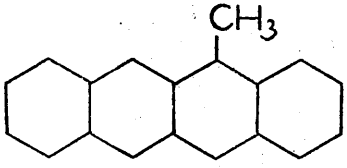
The effect of a methyl substituent in a non-terminal ring has been examined in several other hydrocarbons, but appears to have most effect in the linear acenes. Several possible explanations for these observations are discussed in the light of this evidence.



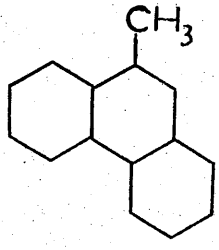
(I)



(II)



(III)



(IV)

Discussicn

During the work involving the n.m.r. investigation of double bond character in methyl derivatives of polycyclic aromatic hydrocarbons, 9-methylanthracene (I) which has only one proton in a position para to the methyl group was synthesised and the n.m.r. spectrum recorded (Fig. I). The methyl signal is a doublet with a surprisingly large separation of 0.8 Hz. This is due to coupling with the para proton H_{10}, which can be shown conclusively by irradiating at the frequency of this proton shown by a dot, causing the methyl doublet to collapse to a narrow singlet. Irradiating at the methyl frequency (300Hz) and recording the aromatic part of the spectrum produces no change in the spectrum apart from the signal at 811 Hz. which sharpens considerably. This can be compared with the value 0.63 Hz of para coupling observed in 2,3,5,6-tetrachlorotoluene (II) Table I.

Similarly the n.m.r. spectrum Fig. 2 of 5-methyltetracene (III) shows the methyl signal as a doublet with a larger separation of 1.0 Hz. This is as large as the coupling observed between the methyl group and the ortho proton in 9-methyl-phenanthrene (IV)[1,2] and indicates a considerable degree of coupling between the methyl and the para proton. Decoupling the methyl signal sharpens the broad singlet at 836 Hz which is assigned to the para proton, H_{12}; no other part of the spectrum is

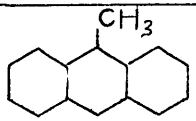
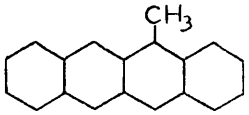
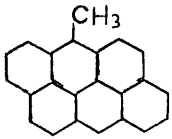
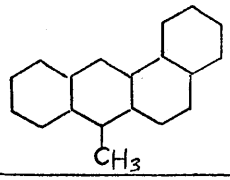
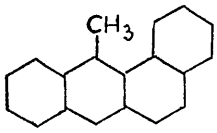
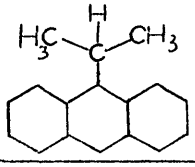
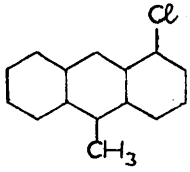
Compound in CS_2	Chemical shift in τ	
	Aromatics	Methyl (J in Hz)
	$H_{2,3,6,7}$ 2.70(m) ; $H_{4,5}$ 2.21(m) $H_{1,8}$ 1.91(m) ; H_{10} 1.89(s. broad)	7.0(d) J= 0.8
	$H_{2,3,8,9}$ 2.75(m) ; $H_{1,7,10}$ 2.15(m) H_4 1.9(m) ; H_{12} 1.64(s) ; H_{11} 1.58 (s) ; H_6 1.29(s)	6.88(d) J= 1.0
	H_{12} 1.63(s. broad)	6.95(s)
	$H_{2',3',4',6,7}$ 2.60(m);H_3 2.54(d) H_4 2.07(d);H_8 2.05(m);H_5 1.85(m) H_1,1.39(m); H_9 1.17(s. broad)	7.04(d) J= 0.65
	$H_{2',3',4',3,4,6,7}$ 2.57(m);H_5 2.3(m) H_{10} 2.09(s. broad);H_8 1.92(m); H_1, 1.69(m)	6.70(s. broad) $J_{CH_3,H_{10}}$=0.65 J_{CH_3,H_1}=0.2
	$H_{2,3,6,7}$ 2.79(m);$H_{4,5}$ 2.27(m); $H_{1,8}$ 1.77(m); H_9 1.97(s. broad)	8.27(d) J= 7.0 methine 6.10 septet J= 7.0
	$H_{,3,6,7}$ 2.40(m);H_8 1.8(m) $H_{4,5}$ 1.60(m);H_9 1.0(s. broad)	6.90(d) J= 0.8

Table 1.

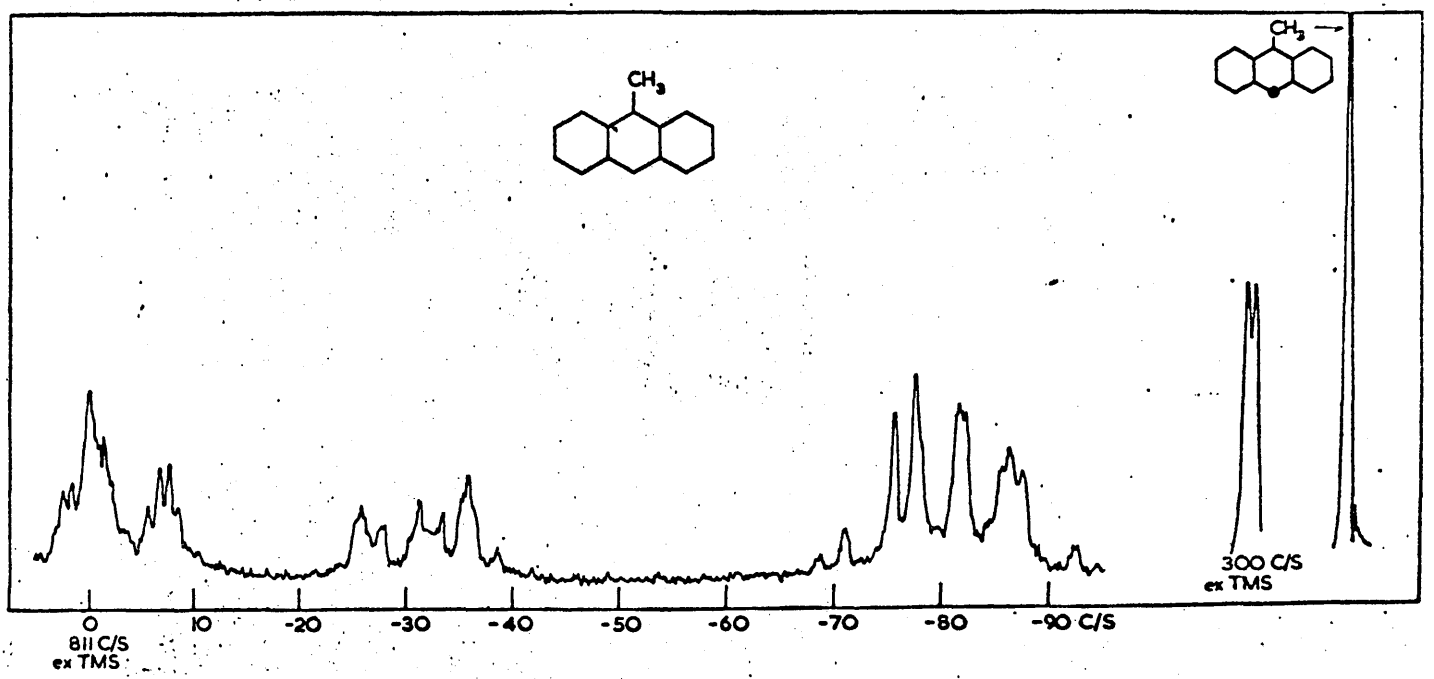


Fig 1. N.m.r. spectrum of 9-methylanthracene in CS_2 at 100MHz.
9-CH_3 300 (d) J=0.8 Hz.; H_{10} 811(s) ; $H_{1,8}$ 809(m) ; $H_{4,5}$ 779(m) ; $H_{2,3,6,7}$ 730(m), Hz.
exo TMS.

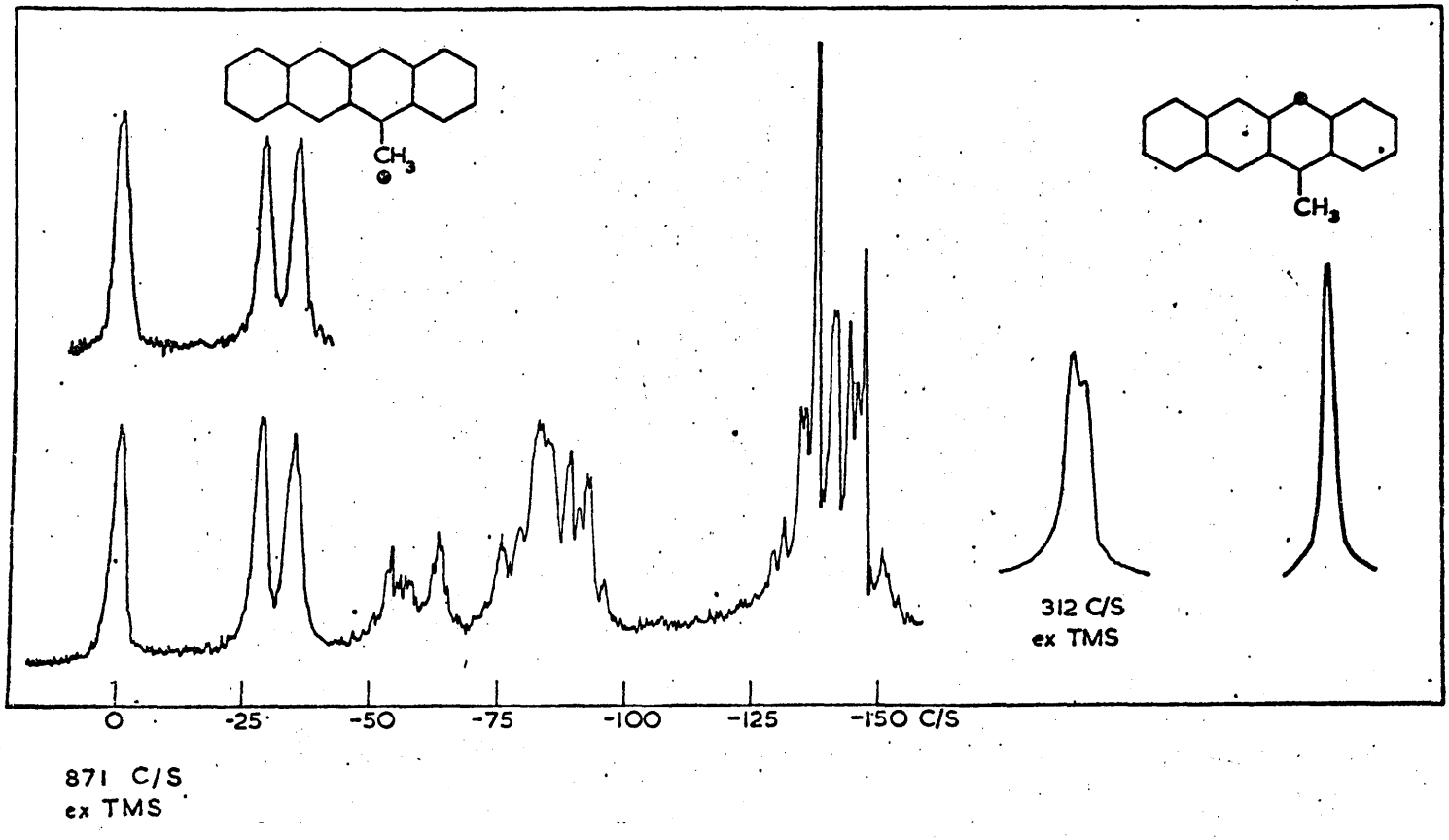


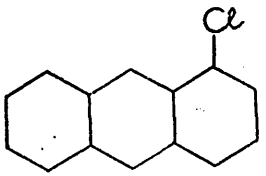
Fig 2. N.m.r. spectrum of 5-methyltetracene in CS_2 at 100MHz.
5-CH_3 312(d) J=1.0 Hz. ; H_6 871(s) ; H_{11} 843(s) ; H_{12} 836(s) ; H_4 810(m) ; $H_{1,7,10}$ 800-770(m) ; $H_{2,3,8,9}$ 710-740(m) Hz. exo TMS.

affected. Decoupling at the proton H_{12} causes the methyl doublet to collapse to a narrow singlet (Fig.2).

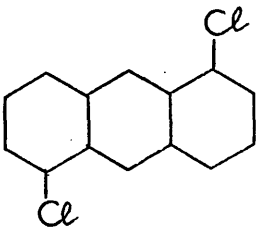
The magnitude of these couplings and the apparent lack of para couplings in the parent hydrocarbons prompted examination of suitably substituted anthracenes and tetracenes, to find if this was a property of the methyl group or inherent in the parent molecule.[3]

Halogen derivatives are ideal for this purpose and the effect of the chlorine atom in 1-chloroanthracene (V) also increases the chemical shift difference between the protons H_9 and H_{10} by 30Hz, allowing decoupling (Table II). Decoupling both the protons H_9 and H_{10} in turn, and examining the remaining proton resonance shows no sharpening of the signals, and there can be no para coupling between these protons. However decoupling the protons H_4, H_5 and H_8 causes considerable sharpening of the H_9, H_{10} proton signals and the reverse process of decoupling the protons H_9, H_{10} sharpens the signals of the protons H_4, H_5 and H_8. There is thus no evidence for para coupling, yet substantial peri cis and/or trans coupling is occuring. This is confirmed with 1,5-dichloroanthracene (VI) where although the protons H_9 and H_{10} are now equivalent and no para coupling would be expected, decoupling of the peri protons H_4, H_8 sharpens the 9,10 proton signal considerably (Table 2).

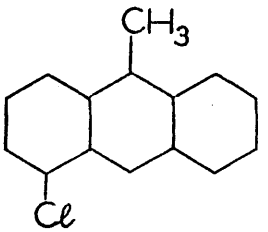
In order to see if the chloro substituent had altered the



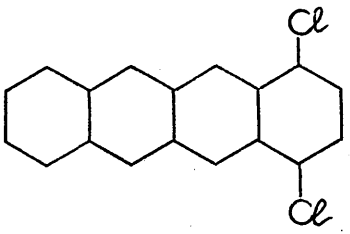
(V)



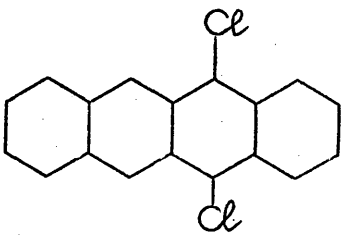
(VI)



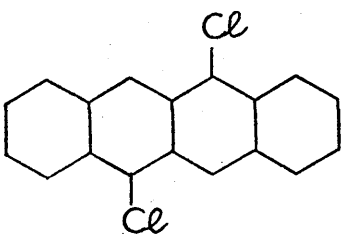
(III)



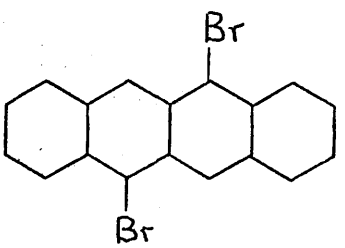
(VIII)



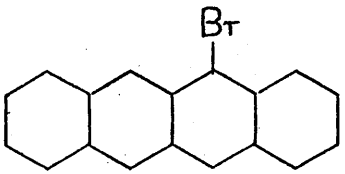
(IX)



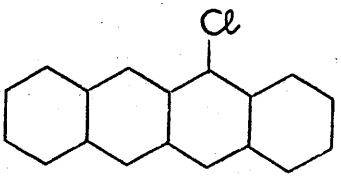
(Xa)



(X)



(XI)



(XII)

electronic arrangement, and to gauge the effect of the methyl group in the para coupling, 1-chloro-10-methylanthracene (VII) was synthesised and the n.m.r. spectrum recorded. The expanded methyl signal (Table I) is a doublet with a separation of 0.8 Hz. which is due solely to para coupling with the proton H_9. Decoupling of this proton causes the methyl doublet to collapse to a singlet. This would seem to indicate that the methyl group is in fact responsible for this large coupling.

Suitably halogenated tetracene derivatives were examined next to find out if this trend was repeated. 1,4-Dichloro-tetracene (VIII) is very suitable as the proton signals are well separated and easily identified. Decoupling the protons H_5 , H_{12} has no effect on the protons H_6 and H_{11} and decoupling these protons does not affect the resonance of the protons H_5 and H_{12}. This indicates the absence of para coupling and peri coupling between the protons of the middle rings of tetracene. However the signal of protons H_5 and H_{12} is narrower and almost one third as intense as that of protons H_6 and H_{11}. This is explained by decoupling the protons H_7 H_{10} which sharpens the proton signal of H_6 and H_{11} to a peak height and half width equal to the proton signal of H_5 and H_{12}. Decoupling the protons H_6 and H_{11} sharpens the proton signal of H_7 and H_{10} and thus confirms the peri coupling observed between the middle ring and terminal rings in anthracene

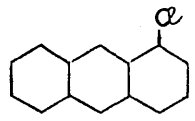
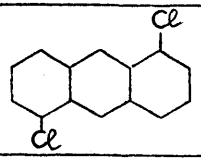
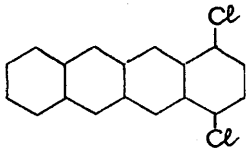
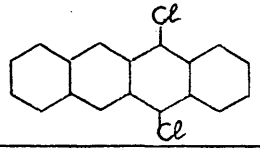
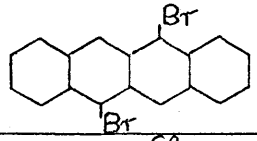
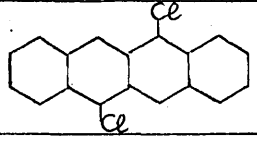
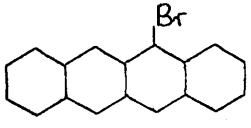
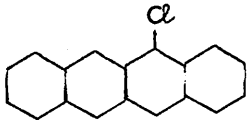
Compound in CS_2	Chemical shift in τ Aromatics
	$H_{2,3,6,7}$ 2.84(m) ; $H_{4,5,8}$ 2.37(m) H_{10} 2.10(s. sharp) ; H_9 1.40(s. sharp)
	$H_{2,3,6,7}$ 2.64(m) ; $H_{4,8}$ 2.10(quartet) $H_{9,10}$ 1.27(s.sharp)
	$H_{2,3}$ 2.73(s.sharp); $H_{8,9}$ 2.69(m) $H_{7,10}$ 2.10(m);$H_{6,11}$ 1.44(s); $H_{5,12}$ 1.07(s. sharp)
	$H_{8,9}$ 2.61(m); $H_{2,3}$ 2.70(m);$H_{7,10}$ 2.00(m); $H_{1,4}$ 1.59(m); $H_{6,11}$ 0.94(s).
	$H_{2,3,8,9}$ 2.57(m); $H_{1,7}$ 2.04(m); $H_{4,10}$ 1.64(m);$H_{6,12}$ 0.90(s).
	$H_{2,3,8,9}$ 2.60(m);$H_{1,7}$ 2.09(m); $H_{4,10}$ 1.64(m);$H_{6,12}$ 1.04(s).
	$H_{2,3,8,9}$ 2.68(m) ;$H_{1,7,10}$ 2.17(m); H_4 1.63(m);$H_{11,12}$ 1.64(s. broad); H_6 1.00(s).
	$H_{2,3,8,9}$ 2.73(m);$H_{1,7,10}$ 2.17(m); H_4 1.70(m);$H_{11,12}$1.60(s. broad); H_6 1.05(s).

Table 2.

(Table II).

This is repeated with 5,12-dichlorotetracene (IX). Decoupling the protons H_7 , H_{10} sharpens the singlet signal of protons H_6 ,H_{11} and the reverse process is true. This means that considerable peri-coupling is present but one cannot say whether cis or trans coupling contributes most to the overall effect (Table II). 5,11-Dibromotetracene (X) offers an opportunity to find which of these two effects is most important.

The protons H_6 , H_{12} adjacent to the bromine atoms are at lowest field and irradiating at this frequency, only sharpens the signals assigned to the protons H_4 , H_{10} which are trans peri to the protons H_6, H_{12}. No change in the signal of the protons H_1 , H_7 is observed when these protons are decoupled, and the reverse process has no effect (Table II). These results are confirmed on examination of the spectrum of 5,11-dichlorotetracene (Table II).

The spectra of the monohalogen derivatives, 5-bromotetracene (XI) and 5-chlorotetracene (XII) also support the above findings. Decoupling the proton H_6 which is peri to the halogen and at lowest field has no effect on the overlapping signals of protons H_{11} and H_{12}. Decoupling at this frequency, similarly affords no change in the signal of proton H_6 . Decoupling protons H_1 ,H_7 and H_{10} sharpens the signal of proton H_6 , but has less effect on the signal of protons H_{11} and H_{12} than

observed in previous cases. This may be due to the fact that the proton H_4 which is trans-peri to the proton H_{12} has almost the same chemical shift and decoupling is not possible. Therefore only the effect of one trans-peri position, that of proton H_7, will affect the overlapping signals of protons H_{11} and H_{12} when the protons H_1, H_7 and H_{10} are decoupled, and the effect will be less evident. (Table II).

The above results indicate that there is no para coupling between the protons in the middle ring, or rings, of anthracene and tetracene, and further there appears to be no coupling at all between the protons of the middle rings of tetracene. There is however appreciable peri coupling between protons on the middle rings and those on the adjacent terminal rings, which appears to operate predominantly by the five bond trans-peri pathway. If any cis-peri coupling is present it is not apparent from the decoupling experiments.

Recently reiterative computer programmes have been compiled which use the best observed couplings from the observed spectra of complicated systems and obtain a calculated fit by repeated adjustment of the couplings. The complete p.m.r. spectrum of naphthalene has been reported recently[5], in which the authors regarded the problem as an eight spin system rather than the isolated AA'BB' system which had hitherto been considered.[6]

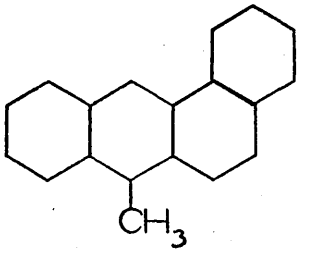
They find that altering the magnitude of the long-range

inter-ring couplings has a considerable effect on the computerised spectrum, and calculate the 1,5 and 1,8 couplings in naphthalene to be as high as 0.85 and 0.45 Hz respectively. The former value seems rather high but the results from our investigations infer that this trans-peri coupling pathway seems most effective in the anthracene and tetracene derivatives. They also quote a value of 0.74 Hz for para coupling between the 1,4 positions which is just less than the 1,5 interaction. Despite this, there is no evidence of para coupling in the cases studied above, although it may not be justified to compare this value for a terminal ring with the middle rings of anthracene and tetracene derivatives.

Nevertheless this does not explain the large value for para coupling between the methyl group and the proton across the ring in the derivatives described.

The spectra of 9-methyltetraphene(XIV) and 10-methyltetraphene (XIII) were recorded to see if this effect was present in a similar system but with an angularly annellated ring. 10-Methyltetraphene (XIII) has a methyl signal which on expansion is a doublet with a separation of 0.65 Hz. Decoupling the methyl signal only sharpens the broad singlet at 1.17τ in the aromatic region and is assigned to the proton H_9. Decoupling at this frequency reduces the methyl to a sharp singlet. (Table 3).

Expansion of the methyl signal of 9-methyltetraphene (XIV)



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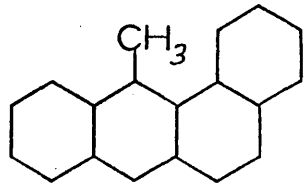

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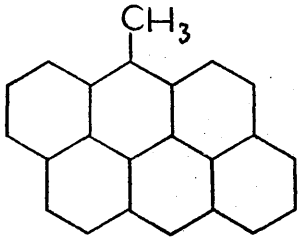

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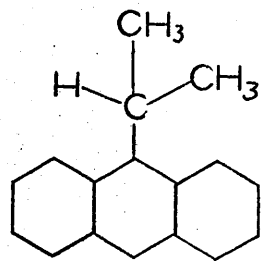

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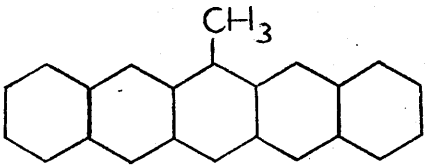

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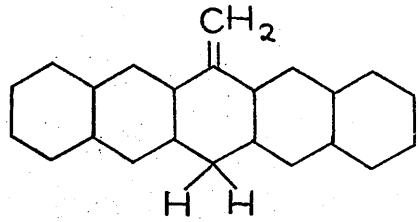

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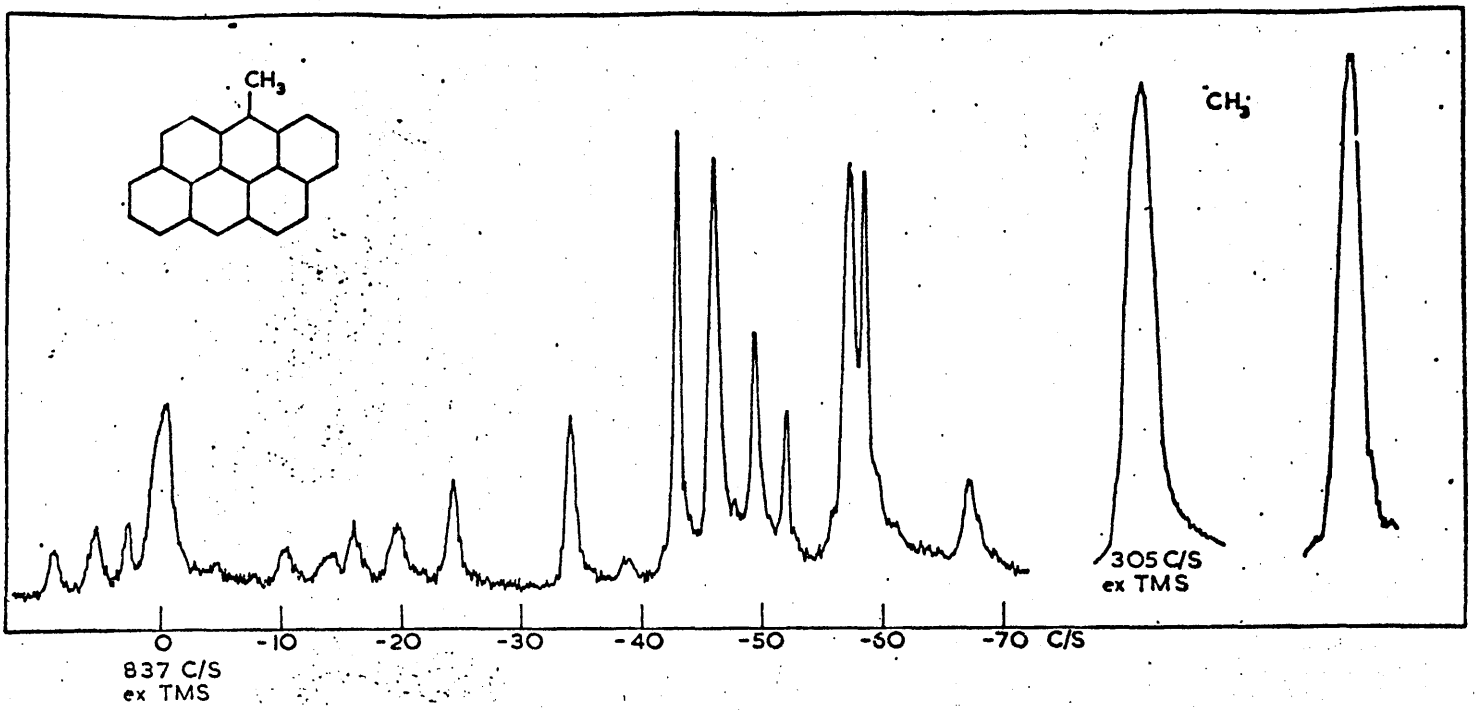


Fig 3. N.m.r. spectrum of 6-methylanthanthrene in CS_2 at 100 MHz.
6-CH_3 305 (s) ; H_{12} 837(s) Hz. exo TMS.

rather surprisingly shows only a broad singlet. Decoupling at the methyl frequency, however, not only sharpens the proton H_{10} at 2.09 τ but also the multiplet at 1.69 τ assigned to proton $H_{1'}$. Irradiating at the frequency of proton $H_{1'}$ results in a doublet methyl signal with a separation of 0.65 Hz, exactly as observed in 10-methyltetraphene (Table 3). Therefore although para coupling is present, the magnitude is less than that observed for 9-methylanthracene.

6-Methylanthanthrene (XV) was synthesised to find if this effect could be extended through more bonds. The spectrum of this derivative (Fig. 3) shows that distance between the methyl group and the proton H_{12} (which corresponds to the para proton in the acenes) is of great importance for the degree of coupling. The methyl signal at 305 Hz is not a doublet as in the previous cases. It sharpens if H_{12} (837Hz) is irradiated. Decoupling of the methyl protons has little influence on the rather complex aromatic spectrum except for the singlet at 837 Hz which sharpens and is assigned to H_{12}. This weak coupling between the methyl and the proton H_{12} is probably not only the result of the greater distance between the two groups but also due to the single bond which crosses the line between them. As before no coupling with the cis-peri protons could be observed.

9-Isopropylanthracene(XVI) was also synthesised to see if there was para coupling involving the methine proton of the

isopropyl group. The methine proton is strongly coupled to the 6 equivalent protons of the geminal methyl groups and appears in the spectrum as a classical septet $J = 7$ Hz at 6.10 τ . The methyl groups resonate as a doublet with a separation of $J = 7.0$ Hz, 8.27 τ . Maximum expansion of the methine signal shows very narrow line widths and there is no indication of para coupling. Decoupling at the methyl frequency reduces the methine signal to a broad singlet with no evidence of splitting. Similarly decoupling at the para proton H_{10} has no effect on the methine signal. However although this compound does not appear to show para coupling it may be masked by the strong methyl-methine interaction, especially as maximum decoupling power was used to remove this coupling and the smaller para-coupling may have been swamped (Table 3).

Finally it is worth noting that an attempt to synthesise 6-methylpentacene (XVII) by the reaction of methylmagnesium-iodide and pentacenone led to a compound with the properties of 6-methylene-6,13-dihydropentacene (XVIII) and not the fully aromatic methyl derivative.[7] However heating a solution of (XVIII) in 1-methylnaphthalene gave a purple solution and the ρ-bands of the fully aromatic pentacene derivative were visible; on cooling the solution became pale yellow once more.[7] It therefore appears that the molecule is more stable in this form and a very plausible explanation based on the annellation principle has been

given.

The above results show that there is considerable coupling between a methyl group and the para proton, in cases where both groups are attached to an otherwise fully substituted ring. The corresponding interaction is not observed between para protons even when their equivalence is removed by suitable asymmetric substitution. One can only conclude that this coupling is due to an interaction of the methyl group with the electronic arrangement in the ring and there appears to be three possible explanations of this phenonenon.

Firstly, the coupling could be simply benzylic coupling transmitted by σ–π interactions along the six bonds between the protons of the methyl group and the para proton as is assumed by conventional theory.[8] This does not explain the larger value obtained in methyl tetracene nor does it explain the apparent lack of coupling in the substituted parent hydrocarbon, especially as this occurs through only five bonds and along the same pathway.

Taking into account the evidence of 5-methylpentacene (XVIII) one could consider that there is a hyperconjugation effect between the methyl group and the ring.[3,9] One could then consider this effect to be enhanced, as shown, by the increase in the magnitude of the coupling from tetrachlorotoluene through anthracene and finally with pentacene as the upper limit, involving complete loss of a proton from the methyl group and addition at the para

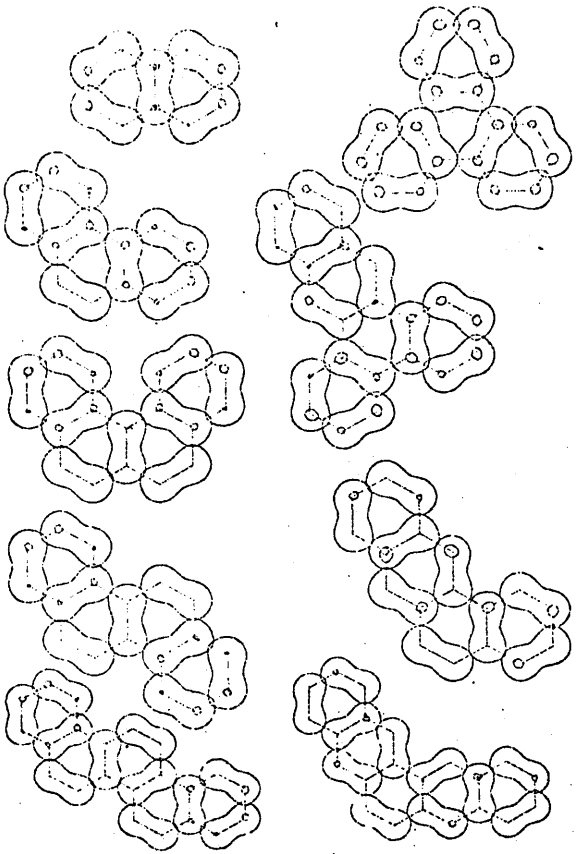


Fig. 4 Kekulé-type localized MO structures

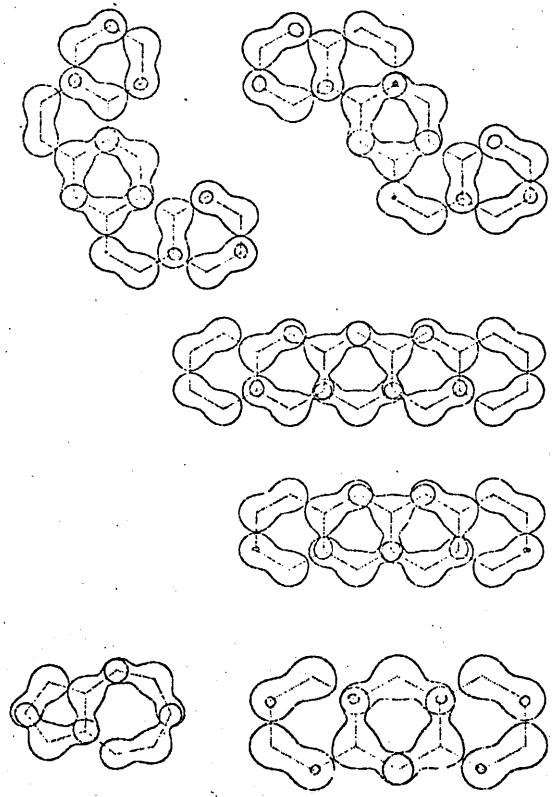


Fig. 5 Non-Kekulé-type localized MO structures

position. In the case of the methyltetraphenes where the coupling is reduced to 0.65 Hz one must assume until further compounds are examined that the angular annellation reduces the effective para coupling, This would at least explain why no para coupling is observed in the parent hydrocarbons.

There is also the possibility of direct interaction across the ring via a para- π- electron bond. Such a bond would not necessarily be weaker than the normal bond between the two π -electrons in a double bond. The absence of a σ-bond will reduce electronic repulsion which would compensate for the increased nuclear repulsion. The increased distance between the carbon atoms forming the bond would also lessen this repulsion. In this way the same magnitude of coupling between the methyl protons and the ortho and para aromatic protons could be rationalised. It could also explain the large observed para coupling 0.55 Hz for 3-methylpyridazine mentioned in the previous chapter. However this still does not explain the lack of para coupling in the parent hydrocarbon and the electron donating methyl group may be required to stabilise this type of situation.

Finally, very recently a paper dealing with the possible interrelation of localised π-orbitals, Pauling bond orders and the origin of aromatic stability, has been published[10] and sheds some light on the above findings. The authors show, from m.o. calculations, that there are basically four types of what

are referred to as 'localised molecular orbitals' present in polycyclic aromatic hydrocarbons. Only two of these four types of orbitals are present in the majority of hydrocarbons, where the Pauling bond order uniquely defines a specific Kekulé structure. These are found to be localised such that they give rise to essentially Kekulé type structures (Fig. 4.)

However for several other hydrocarbons, including anthracene, tetracene and pentacene the other types of orbitals are also involved, and in the acenes they are located in the central rings (Fig. 5).

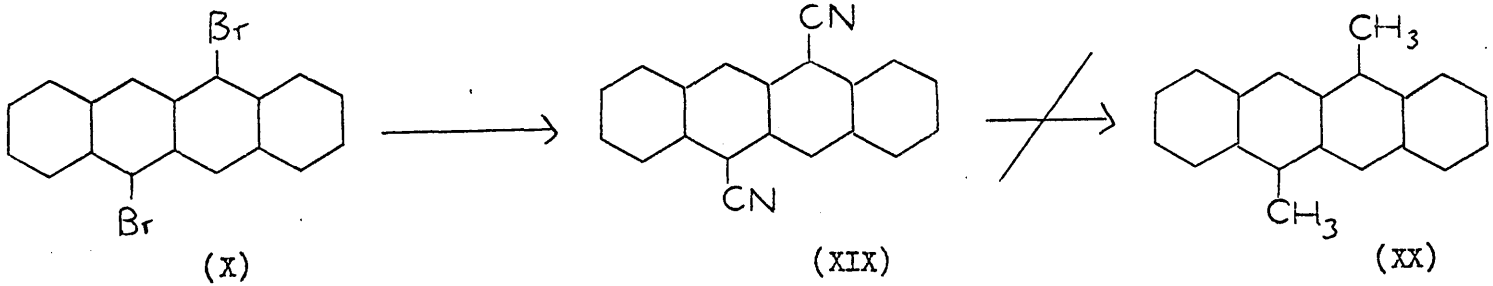
Therefore this offers a possible explanation for the different coupling values and in fact the general chemical reactivity of the middle rings of the acenes compared with the terminal rings. Also as the localised structure calculated for tetraphene falls into the former category, this would explain why the coupling constant is of the same order of magnitude as in tetrachloro-toluene, and smaller than that observed for the methylacenes.

Experimental Discussion

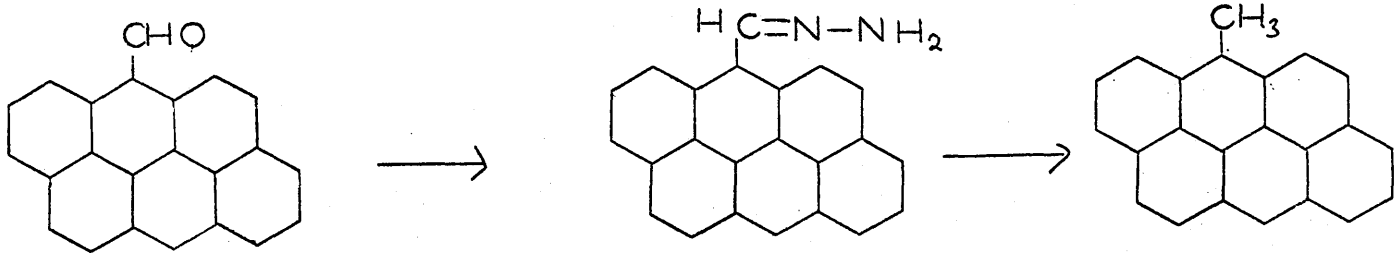
The main part of the synthetic work in this chapter involved attempts to obtain 5,11-dimethyltetracene (XX) for comparison of the methyl signal with that of 5-methyltetracene (III). 5,11-Dibromotetracene (X) was readily formed by direct bromination of tetracene using the method of Marschalk and Stumm.[11] It was hoped to replace the bromine atoms by cyanide groups[12] and to reduce these to the required hydrocarbon with hydrazine hydrate. Although the method was successful in previous work, only traces of the required derivative were found when the dicyanide derivative (XIX) was treated with hydrazine hydrate, and this method was abandoned.

Instead, dibromotetracene was first treated with n-butyllithium and the resulting solution reacted with dimethyl sulphate. This method gave excellent yields of 1,2,5,6-tetramethylnaphthalene from corresponding 1,5-dibromo-2,6-dimethylnaphthalene. However there was no evidence of the required dimethyltetracene from the U.V. spectrum of the crude product.

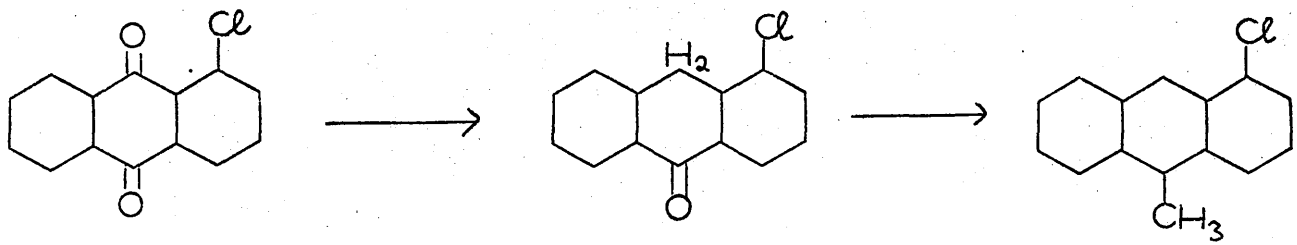
A literature survey showed that very few methyltetracenes had been synthesised and those which have a methyl substituent in one of the middle rings such as 1,6-dimethyltetracene and especially 5,12-dimethyltetracene are sensitive to oxidation.[13] Although 5-methyltetracene is reasonably stable, failure to obtain the dimethyl derivative may be due to a similar sensitivity of



(X) (XIX) (XX)



(XXI) (XXII) (XV)



(XXIII) (VII)

this molecule to oxidation.

6-Methylanthanthrene (XV) was synthesised in a similar manner to that employed by Buu-Hoi and Lavit[14] with the additional improvement of converting the anthanthrene-6-aldehyde (XXI) to the hydrazone (XXII) thus removing any unreacted anthanthrene. The hydrazone was then reduced in the usual manner to give the required hydrocarbon.

Surprisingly a literature survey revealed that 1-chloro-10-methylanthracene (VII) had not been synthesised. This could readily be achieved by reaction of methylmagnesiumiodide and 1-chloroanthrone, and chromatographing the resulting crude product.

9-Isopropylanthracene (XVI), and 9-methylanthracene (I) were synthesised exactly as reported in the literature[15,16], and the two hydrocarbons were purified by chromatography. 5-Methyltetracene (III) had been synthesised previously by reaction of methyl-magnesiumiodide and tetracenone.

The remaining halogen derivatives of tetracene and anthracene were from the collection of Professor Clar and the two methyl-tetraphenes were very kindly gifted by Professor M.S. Newman.

EXPERIMENTAL

5,11-Dibromotetracene (X).

This compound was prepared exactly as described by Marschalk and Stumm[11] and crystallised as long thin needles from xylene.

5,11-Dicyanotetracene (XIX).

Dibromotetracene (2g.), cuprous cyanide (1.2g.) and pyridine (1.1g.) were mixed together and heated at 210° in a sealed tube for 15 hours. The dark black red solid mixture was treated with a mixture of benzene and dil. ammonia and extracted several times with benzene. The extracts were filtered and the benzene layer further washed with ammonia, dilute hydrochloric acid and washed thoroughly with water and dried. Concentration of the benzene solution yielded small dark red needles (0.1 gm.) which were further purified by sublimation. m.pt. 309-311° which dissolved in concentrated sulphuric acid forming an orange solution.
M.S. molecular ion m/e=278; calculated M.W.=278.

Found		C=86.15%, H=3.77%, N=9.90%.
$C_{20}H_{10}N_2$	requires	C=86.34%, H=3.59%, N=10.07%.

Attempted reduction of 5,11-dicyanotetracene.

The dicyanide (100 mgs.), hydrazine hydrate (5ml.) and xylene (2ml.) were heated in a sealed tube at 200° for twenty hours. The resulting brown yellow solid was filtered from the solvent which was diluted with water and the xylene layer separated. The xylene solution and the xylene extract of the solid were combined, dried concentrated and chromatographed on Grade I neutral alumina. Concentration of the resulting fractions did not yield the required hydrocarbon, but a small amount of yellow oil which was not characterised..

6-Formylanthanthrene(XXI).

Anthanthrene (4 gm.), N-methylformanilide (2.4 gm.) and phosphorus oxychloride (2.8 gm.) in o-dichlorobenzene (8ml.) were gently refluxed for four hours. The sticky green reaction mixture was poured into a solution of sodium acetate and stirred with further o-dichlorobenzene (50ml.). After steam distilling off the dichlorobenzene the dark green solid (3.8 gm.) was filtered off and dried.

Anthanthrene-6-hydrazone(XXII).

The crude aldehyde (2 gm.) was dissolved in boiling pyridine (100ml.)and hydrazine hydrate (50%,20ml.) was added. After boiling for 5 minutes, water (50ml.) was added. This dilution ensures that unreacted anthanthrene is not carried on through

the further stages. The hot solution was filtered from the precipitated residue and the hydrazone itself precipitated by addition of a further quantity of water (300ml.). The light brown hydrazone(1.1gm.) was filtered and dried. m.pt. 195° (dec) and dissolved in concentrated sulphuric acid with a deep purple colouration.

Found	C=86.72%, H=4.55%, N=8.58%
$C_{23}H_{14}N_2$ requires	C=86.77%, H=4.43%, N=8.80%

6-Methylanthanthrene (XV).

The above pure hydrazone (0.35gm.) was dissolved in diethylene glycol (35ml.), hydrazine hydrate (2ml.) was added and the mixture heated to 210° under nitrogen. After cooling to 150° potassium hydroxide (0.4gm.) was added and refluxed for 30 minutes. The formed water was removed from the condenser and the temperature allowed to rise to 220°. The mixture was cooled to 100° and the hydrocarbon precipitated with water. The yellow-green precipitate was dissolved in xylene, the solution boiled to remove water and chromatographed over Grade I neutral alumina. Concentration of the solution yielded orange leaflets (150 mgs.) which had m.pt. 188-190°(Lit.[14] m.pt. 192°) and dissolved in concentrated sulphuric acid forming a brown solution.

Found	C=94.88%, H=4.93%
$C_{23}H_{14}$ requires	C=95.17%, H=4.83%

1-Chloroanthrone (XXII).

This was prepared exactly as described by Barnett and Matthews[17] and recrystallised from ethanol.

1-Chloro-10-methylanthracene.(VII).

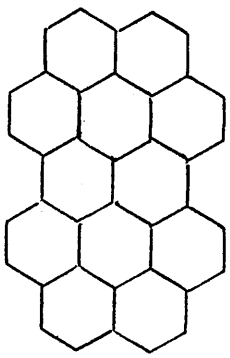
The above anthrone (3.6 gm.) dissolved in dry benzene (20ml.) was added dropwise to an ethereal solution of magnesium (2gm.) and methyliodide (10g) previously prepared. The clear pale brown solution became red on addition of the anthrone. After refluxing gently for one hour the green yellow solution was cooled and the mixture decomposed with ice and dilute acetic acid. The organic layer was refluxed for one hour with acetic acid (30ml.) and a few drops of concentrated hydrochloric acid to convert the intermediate carbinol to the required hydrocarbon. Water was added to the mixture and the product extracted with xylene. The xylene solution was washed with water, dried and concentrated. Chromatography of this solution over Grade I neutral alumina, eluting with light petrol (60-80°) gave a pale yellow green band with a purple fluorescence. Concentration of these fractions gave pale yellow crystals (1.4g.) which on recrystallisation from ethanol gave slender pale yellow prisms m.pt. 72-73° and dissolved in concentrated sulphuric acid with an olive green colour.

Found C=79.16%, H=4.72%

$C_{15}H_{11}Cl$ requires C=79.46%, H=4.84%

CHAPTER 3.

HYDROCARBONS ISOLATED from the DIMERISATION of 6-NAPHTHANTHRONE.



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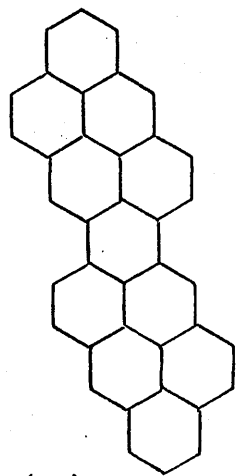

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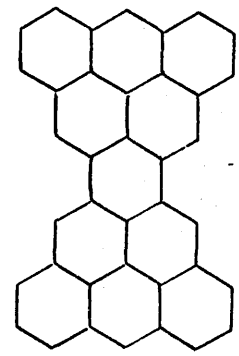
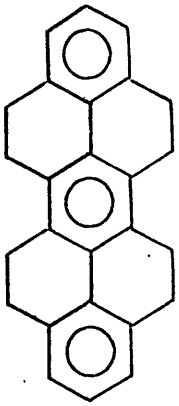


(III)

INTRODUCTION

A more rigorous investigation of the products formed by reductive dimerisation of 6-naphthanthrone was undertaken. Along with several previously characterised hydrocarbons, two new aromatic hydrocarbons were isolated. The highly condensed, circobiphenyl (I) and a purple hydrocarbon which has tentatively been assigned the structure dibenzisoviolanthrene (II) on the basis of the U.V. spectrum. However it shows an unexpected reactivity with maleic anhydride which rather favours the structure 1,14:3,4:7,8:10,11-tetrabenzoperopyrene (III).



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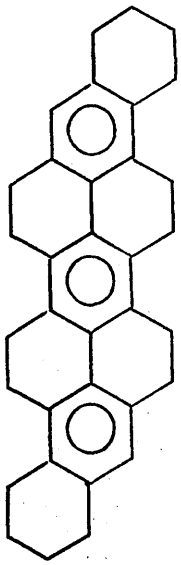

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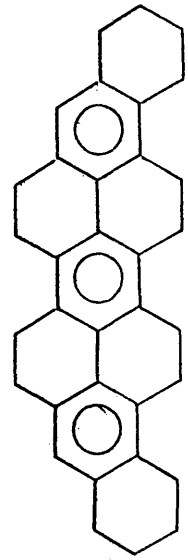

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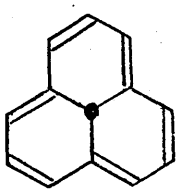

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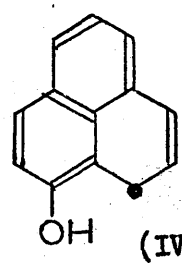

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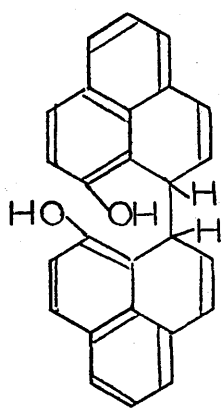


(V)

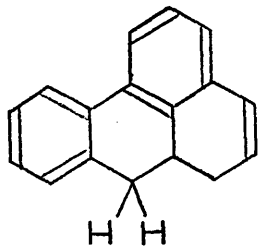
Discussion

An interesting group of hydrocarbons are those which can be considered to be derivatives of the hydrocarbon peropyrene. This hydrocarbon which can in turn be considered the next higher homologue of pyrene is best formulated with three aromatic sextets as shown. (1)

The main interest over the years has been focused on two dibenzoperopyrenes, the isomeric violanthrene (11b) and isoviolanthrene (11a), as their corresponding quinones and the derivatives of these quinones, are of great importance in the dyestuffs industry.[1]

By far the simplest route to these hydrocarbons is an extension of the main method of synthesising peropyrene, namely by dimersation and condensation of two perinaphthyl radicals.[2] (111) The perinaphthene molecule is triangular shaped and cannot exist as a stable hydrocarbon, as one cannot write Kekulé structures which accommodate all the electrons. It therefore exists in the form of a radical, as the hydroderivative perinaphthene, or in the oxygenated form as perinaphthone. The perinaphthyl radical is fairly stable, much more so than the naphthyl radical and can even be distilled without decomposition.[3] This stability is thought to derive from the structure with the extra electron in the centre (111) and the cyclic conjugation of the six double bonds round the periphery.

The intermediate radical (1V) can be readily generated by zinc dust melt of perinaphthone and the extra valency of each molecule



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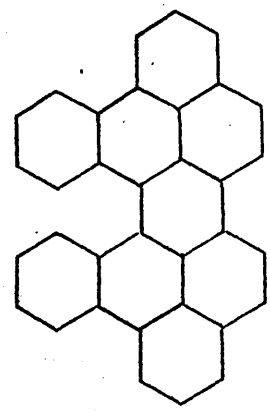

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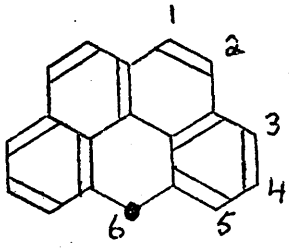
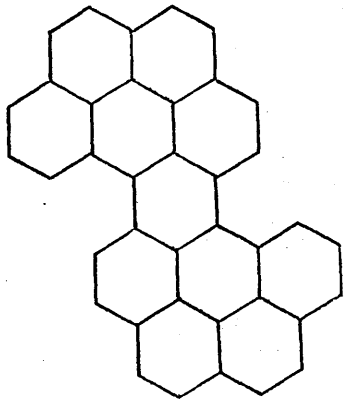


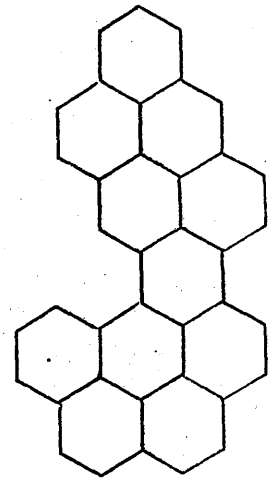
(VIII)

$\#\,|a|_{calc} = 27.4\,|\rho_{McL}|$ Table 1

Atom *	ρ_{HMO}	ρ_{McL}	$\|a\|_{calc}$ #	$\|a\|_{obs}$ ##
1	0	-0.0377	1.03	1.13
2	0.0606	0.0806	2.21	2.40
3	0.1364	0.1950	5.34	5.54
4	0	-0.0569	1.56	1.55
5	0.1364	0.1857	5.08	5.25
6	0.2424	0.3527	9.66	8.36



(IX)

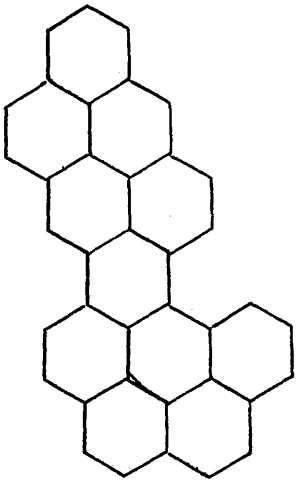


(X)

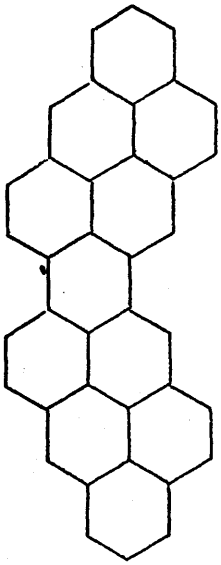
can combine to give the intermediate[2] (V), which on further condensation yields the stable aromatic hydrocarbon peropyrene. There is only one possible dimeric product from this reaction as the perinaphthyl structure is symmetrical.

Extension of this synthetic method to form benzologues of peropyrene naturally results in mixtures of the possible isomers. The benzanthryl molecule like perinaphthene cannot be formulated with Kekulé structures and also exists in the form of a radical, as the hydroderivative benzanthrene (VI), or the oxidised form benzanthrone.[4] A similar treatment of benzanthrone with zinc dust forms the intermediate dimer and condensation results in a mixture of dibenzperopyrene isomers. All the possible dibenzo-peropyrenes apart from (VII) have been synthesised, mainly by using chloro and bromobenzanthrone derivatives which lead unambiguously to specific isomers. They have been characterised from their U.V. spectra and by comparison with those isomers which were synthesised unambiguously.[5]

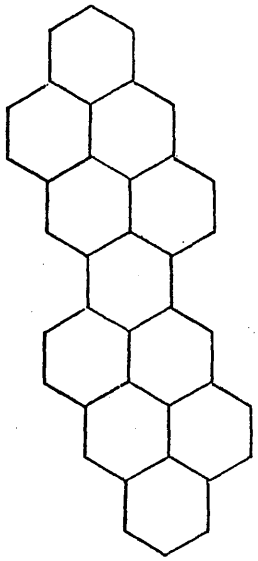
In order to obtain the next higher benzologues of peropyrene, dimersation of naphthanthrone was investigated by the general method outlined. Recently the electron paramagnetic resonance of the naphthanthryl radical (VIII) has been examined.[6] The analysis of the resulting spectrum allowed the observed coupling constants to be compared with those obtained from spin density calculations. These results are shown in Table 1 and allow an 'a priori' prediction of the most likely derivatives on the basis of electron density distribution of the radical over the naphthanthryl molecule.



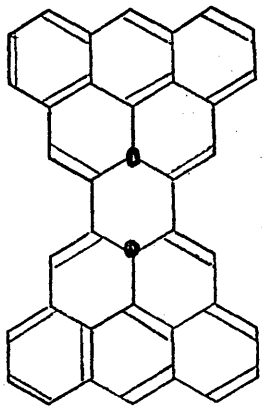
(XI)



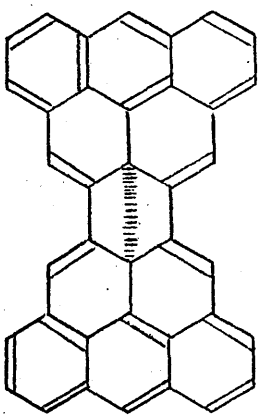
(XII)



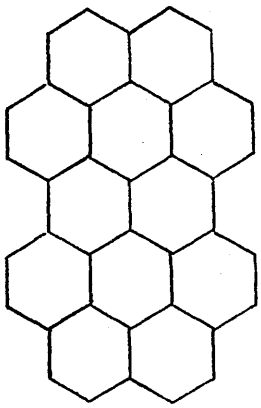
(XIII)



(XV)'



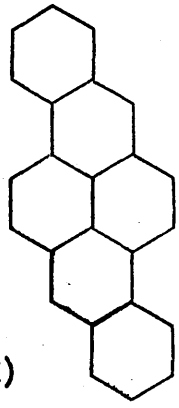
(XV)



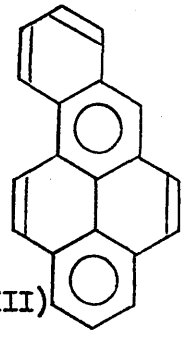
(XVI)

The most favourable position is at carbon 6, and carbons 3 and 5 have the next highest electron density. This is certainly borne out by the products from the preliminary investigations of Clar and coworkers[7] who isolated dinaphtho-(7'.1':1.13);(1".7":6.8) - peropyrene (1X) as the main component from a zinc chloride, zinc dust melt of 6-naphthanthrone. They also isolated another isomer which was assigned the structure (X) on the basis of the U.V. spectrum.[7]

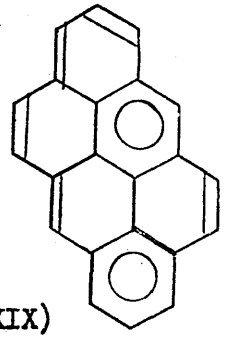
The possible isomers derivable from dimerisation and condensation of 6-naphthanthrone are shown in structures (1X to XV1). Apart from (XV) all are possible on the basis of the spin density calculations mentioned above.[6] A closer investigation of (XV) shows that this molecule, although less likely to be formed by this method has the same inherent problem as posed by the triangulene structure. It is not possible to write Kekulé structures for this molecule without having two electrons left over which cannot be accommodated in a conventional bond. An attempted synthesis of triangulene itself, proved that it existed as an unstable diradical which spontaneously polymerised when formed.[8] However the possibility arises in structure (XV) of combining these two free valencies, not in a diradical structure (XV)', but by forming a Dewar-π - bond across the middle ring as shown (XV). This would allow Kekulé structures for the remainder of the molecule and would confer stability to the molecule. Partial evidence for this structure has been obtained in the work outlined in this chapter, however an attempted synthesis of this skeleton by another route and a fuller



(XVII)



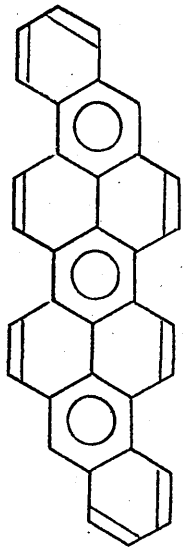
(XVIII)



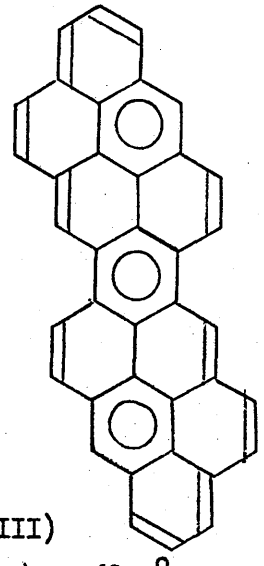
(XIX)

λ_p = 3860 $\xrightarrow{+470}$ 4330 Å

λ_β = 2970 $\xrightarrow{+130}$ 3100 Å



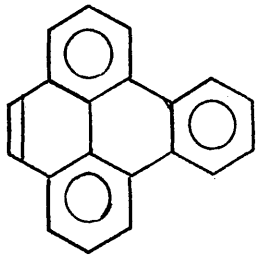
(IIa)



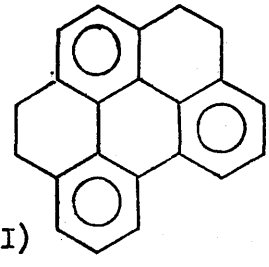
(XIII)

λ_p = 5220 $\xrightarrow{+460}$ 5680 Å

λ_β = 3620 $\xrightarrow{+140}$ 3780 Å



(XXI)



(XXII)

λ_p = 3315 $\xrightarrow{+560}$ 3870 Å

λ_β = 2890 $\xrightarrow{+140}$ 3030 Å

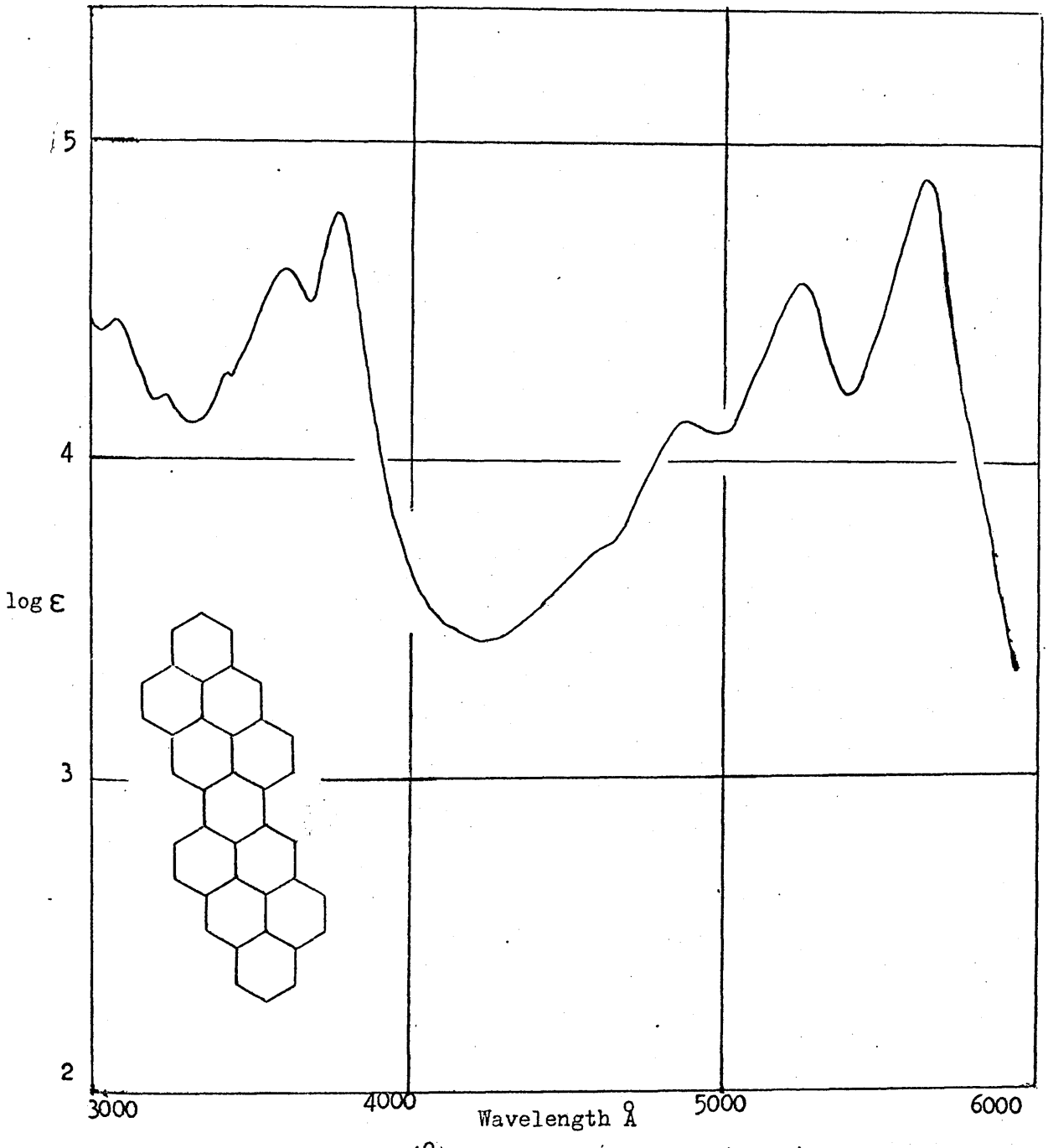


Fig.1 Absorption max. (Å) and log ε (in parentheses)
Dinaphtho - (1',7':2,4); (1",7":9,11) - peropyrene in xylene
ρ: 5680(4.86), 5250(4.54), 4890(4.11); β : 3790(4.76), 3610(4.59);
β′ : 3080(4.43).

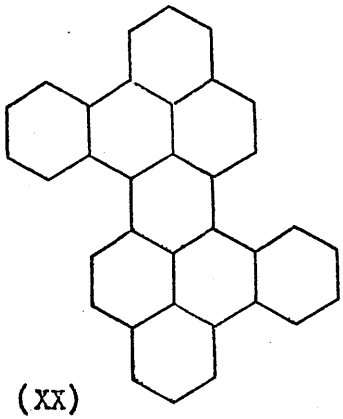
discussion follows in the next chapter.

Besides the already known hydrocarbons (1X) and (X)[7], two new hydrocarbons, circobiphenyl[9] (XV1)and a purple hydrocarbon which has been tentatively assigned the structure of dibenzisoviolanthrene (X111), were isolated in a pure state from the zinc dust treatment of 6-naphthanthrone. A red hydrocarbon which from analysis results and mass spectral data appears to be a hydroderivative of this series has also been isolated.

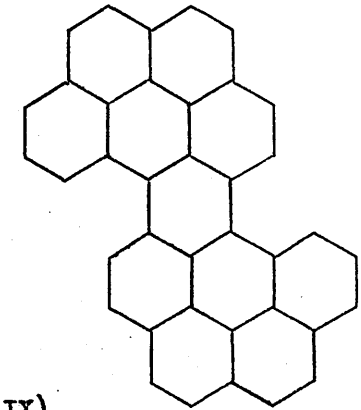
The normal physical tests on this purple hydrocarbon; its mass spectrum and analysis, showed that it had the required formula $C_{38}H_{18}$ and the U.V. spectrum in xylene is shown in Fig.1. Examination of the possible structures in the light of the U.V. spectrum favoured the dinaphtho-(1'.7':2.4);(1".7":9.11)-peropyrene (X111) which is the dibenzologue of isoviolanthrene. The very sharp β-band at 3780Å is typical of a molecule with this condensed acene type of structure as in 3,4:8,9 -dibenzopyrene (XV11). Consideration of the shifts in the bands going from 3,4 - benzopyrene (XV111) to anthanthrene (X1X) by addition of an ethylene bridge show a red shift of the β-bands of 130Å and the ρ-bands by 470Å.

The corresponding shifts comparing the spectrum of isoviolanthrene (11a) with that of the purple hydrocarbon (X111) are 140Å for the β-band and 460Å for the ρ-band, very similar to the above.

A direct comparison of the two series, i.e. the dibenzoperopyrenes and the dinaphthoperopyrenes is possible from the spectra of the two known compounds dinaphtho (7'.1':1.13);(1".7":6.8) - peropyrene (1X)



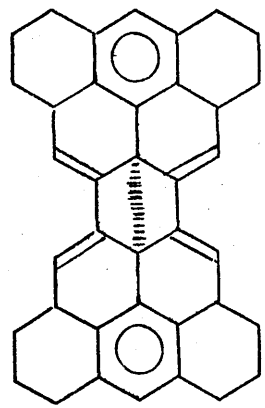
(XX)



(IX)

λ_p = 4450 $\xrightarrow{+\ 650}$ 5100 Å

λ_β = 3480 $\xrightarrow{+\ 190}$ 3670 Å



(XV)

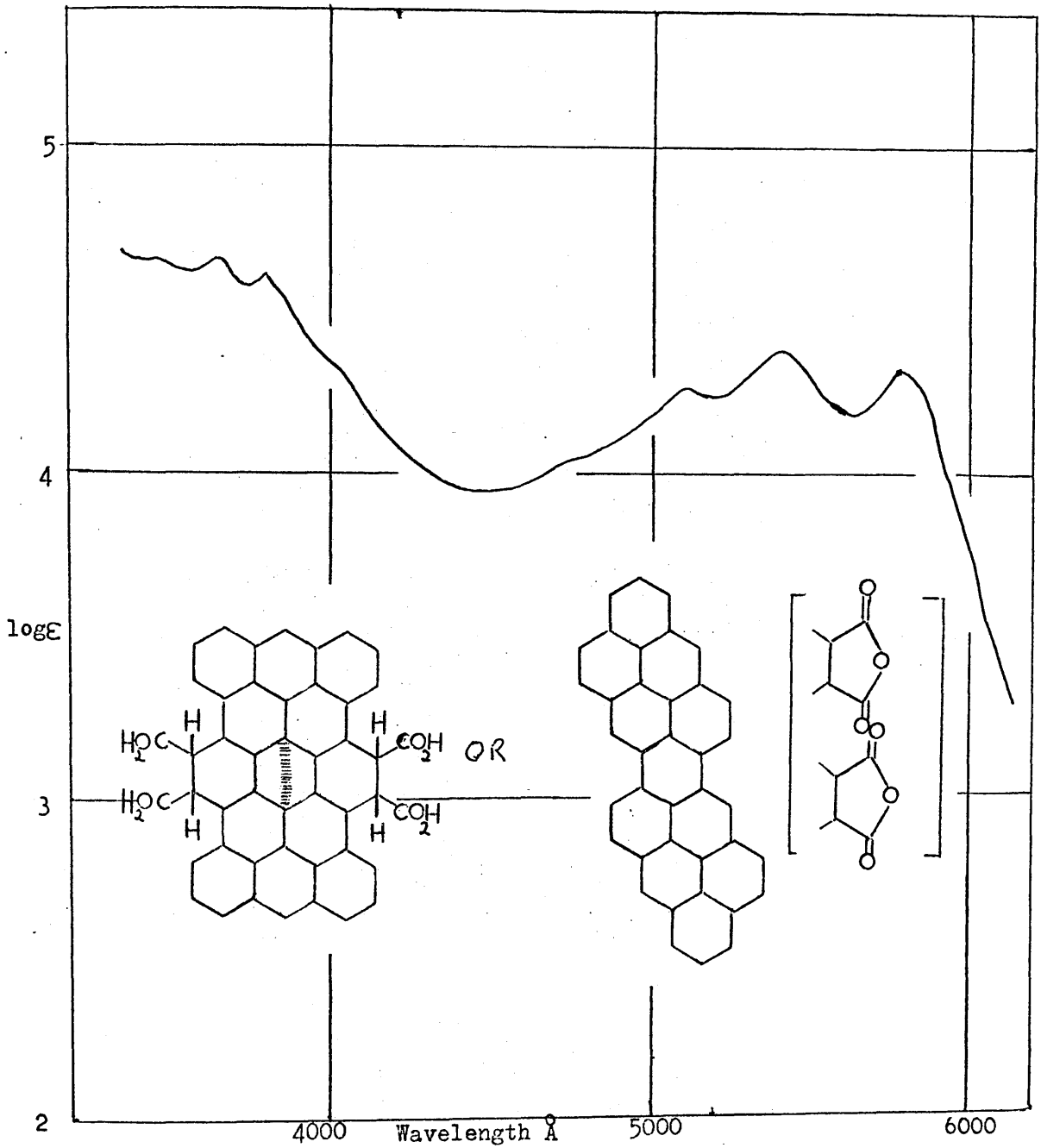
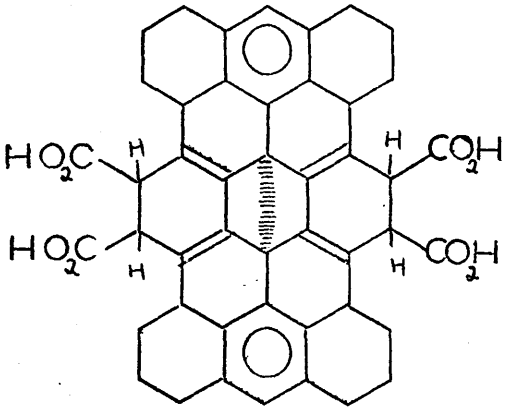


Fig.2 Absorption max (Å) and log ε (in parentheses)
Tetracarboxylic acid adduct in diethylenetriamine p: 5810(4.29), 5430(4.36), 5730(4.24); β : 3800(4.60), 3670(4.66).

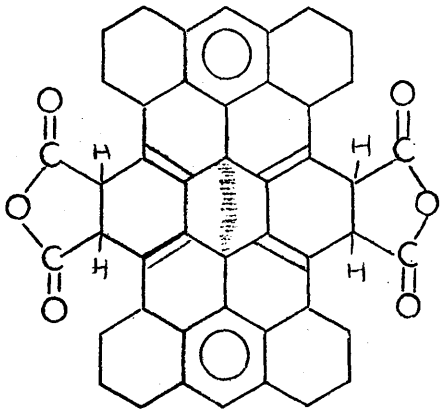
and 4,5:11,12-dibenzoperopyrene (XX) as shown. The addition of two ethylene bridges to (XX) to form (1X) is accompanied by a red shift of the β-band of 190Å and the ρ-band by 650Å. The corresponding shifts observed on addition of an ethylene bridge to 1,2-benzopyrene (XX1) to form 1,12-benzoperylene (XX11) are 140Å to the red for the β band and 560Å for the ρ-band.

Overall these shifts show that the change in the spectra in going from isoviolanthrene to the new purple hydrocarbon fit this pattern and support the assignment of structure (X111), dibenz-isoviolanthrene to the hydrocarbon.

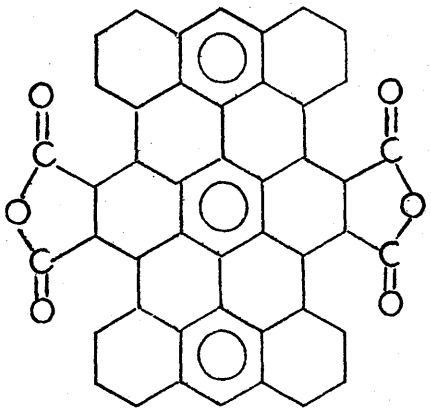
However very surprisingly this hydrocarbon reacts readily with maleic anhydride without a dehydrogenating agent such as chloranil or iodine to give a purple tetracarboxylic acid whose U.V. spectrum in diethylenetriamine is shown Fig. 2 . The ρ-bands have shifted by 130Å to the red and the β-bands by only 10Å in comparison with the hydrocarbon Fig. 1 . The shape of the spectrum has altered very little and must involve a similar electronic conjugation to that in the hydrocarbon. This acid can be readily converted to the anhydride by refluxing with acetic anhydride. Examination of the electronic structure of dibenzisoviolanthrene (X111) indicates that the molecule should not undergo benzogenic diene synthesis even once, let alone twofold addition.[10] In fact none of the possible isomers shown should be capable of reaction with maleic anhydride apart from 1,14:3,4:7,8:10,11- tetrabenzoperopyrene (XV) with the Dewar-π - bond.



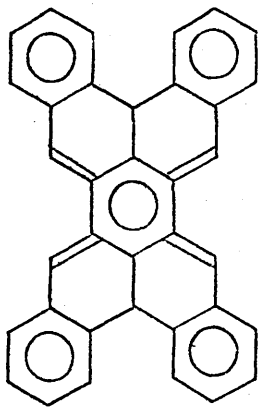
(XVa)



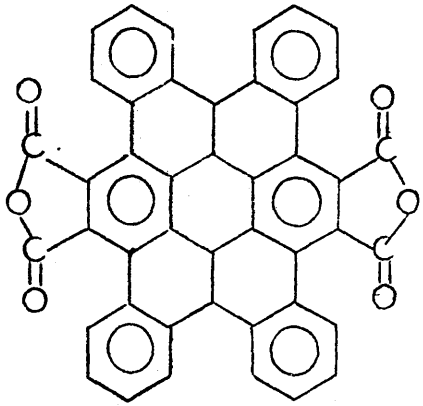
(XVb)



(XVc)



(XIV)



(XIVa)

The arrangement of the bonds in this molecule indicate that twofold addition of maleic anhydride would occur to give the compounds (XV a,b,c,) analogous to the case of 1,14:3,4:7,8:10,11-tetrabenzoperylene (XIV) which forms the diadduct (XIVa) immediately under similar conditions.[11]

Attempts to dehydrogenate the purple adduct to obtain the fully aromatic molecule (XVc) one might expect from this structure (XVa) were unsuccessful, although a green fringe was observed in the flask which gave a very weak band at 8140Å in trichlorobenzene. Similarly attempts to decarboxylate the adduct resulted in dissociation to the hydrocarbon.

Although neither of the isomeric violanthrenes should react according to their electronic structure, they were both refluxed for 30 mins. with maleic anhydride and a crystal of iodine. No reaction could be found in the case of violanthrene. However a shift from 5180Å to 5300Å in the ρ-bands of the alkali extract from the isoviolanthrene reaction indicated the presence of an adduct. Only a very small amount of product (< 1mg.) was present however; the vast majority of the hydrocarbon remaining unchanged after refluxing even for several hours and the subsequent analysis did not fit any plausible structure being far too low in carbon. Increasing the amounts of reagent did not increase the yield of the adduct.

If one assumes the dibenzisoviolanthrene structure (XIII) for the purple hydrocarbon the above can be used as evidence that it might indeed also react with maleic anhydride, but the very small yield

of the above adduct compared with almost total reaction of the purple hydrocarbon is certainly not conclusive.

The evidence against the structure (XIII) reacting with maleic anhydride is based on the application of the aromatic sextet,[12] whereby dibenzisoviolanthrene (XIII) is best formulated with three inherent sextets. This arrangement does not give rise to localised dienophilic regions and therefore the molecule would not be expected to react with maleic anhydride. The analogy has also been drawn from the M.O. calculations of Polansky and Derflinger.[10] Although they did not consider this molecule, their work supports the application of the aromatic sextets to this type of situation.

Hence an isomer of the $C_{38}H_{18}$ series has been obtained in a pure state, and readily reacts with maleic anhydride. Its U.V. spectrum favours the dibenzisoviolanthrene structure, yet its reactivity with maleic anhydride fits the tetrabenzoperopyrene (XV) structure. In order to try and clear up this problem a separate synthesis of tetrabenzoperopyrene (XV), was undertaken and will be described in the next chapter. Attempts to form the quinones of the dibenzisoviolanthrenes, by alkali fusion of naphthanthrone, are also described in the experimental discussion which follows.

The hitherto unknown circobiphenyl (XVI) was also isolated, its existance being favourably predicted from the spin density calculations on the naphthanthryl radical.[6] It is a highly

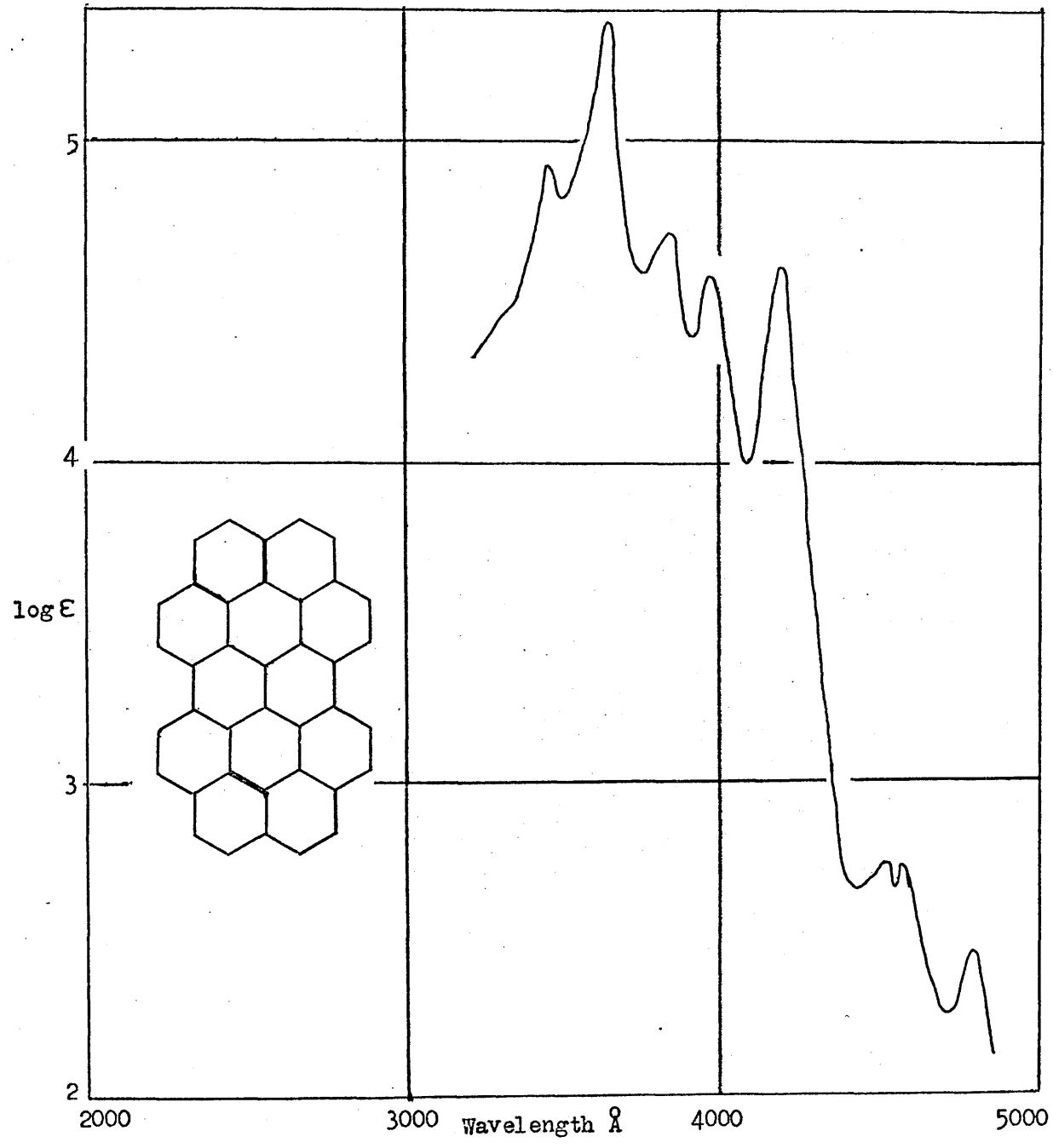
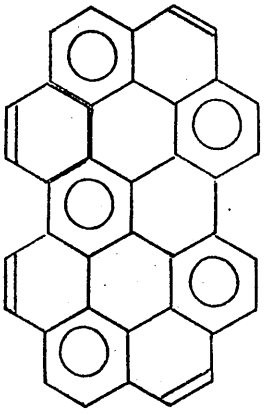
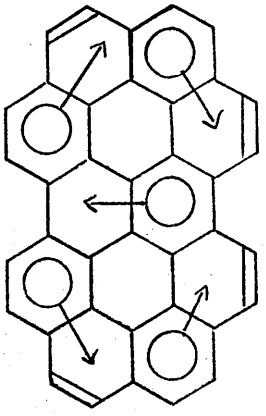


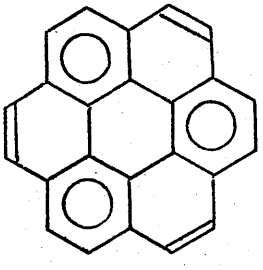
Fig.3 Absorption max (Å) and log ε (in parentheses)
Circobiphenyl in trichlorobenzene α : 4810(2.45), 4590(2.72), 4530(2.73); ρ : 4190(4.60), 3970(4.58), 3840(4.72); β : 3640(5.36). 3450(4.92).



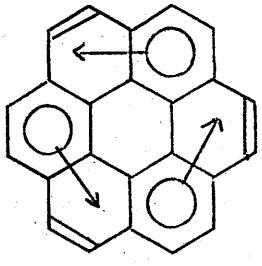
(XVI)



(XVIa)

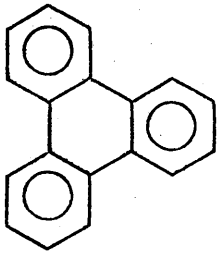


(XXIII)

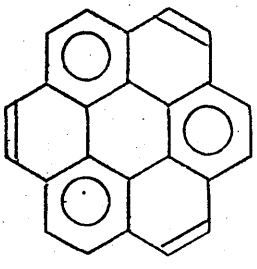


(XXIIIa)

(XXIV)



(XXIII)



$\lambda\beta$ = 2570 $\xrightarrow{+480}$ 3050 Å

condensed hydrocarbon with a high melting point, and is best formulated with five aromatic sextets and four double bonds as shown (XVI) and (XVIa). It can be considered as a double coronene and there must be complete mobility of the sextets[13] as in coronene itself (XXIII), (XXIIIa). This analogy with coronene thus gives rise to the possibility of superaromaticity which is manifested in coronene by the shift to low field of the single proton signal, compared with normal aromatic proton signals.[14] Attempts have been made to record the n.m.r. spectra using high temperatures and hexamethylbenzene as solvent, to overcome the very low solubility. The spectra is shown in Fig.3a , however there is some ambiguity concerning the ratio of the signals, which appear to vary from run to run. Circobiphenyl has an orange red phosphorescence of long lifetime when irradiated in solid solution. The U.V. spectrum in trichlorobenzene is shown in Fig. 3 and is very similar to that of coronene with the appropriate red shift, but with less fine structure in the α-bands.

Over the years Clar and coworkers have derived annellation series for groups of similar aromatic hydrocarbons, which allow predictions of the U.V. spectra of new hydrocarbons, and an insight into the electronic conjugation within these molecules. These effects are remarkably consistent for smaller molecules, however they become more complicated when dealing with larger

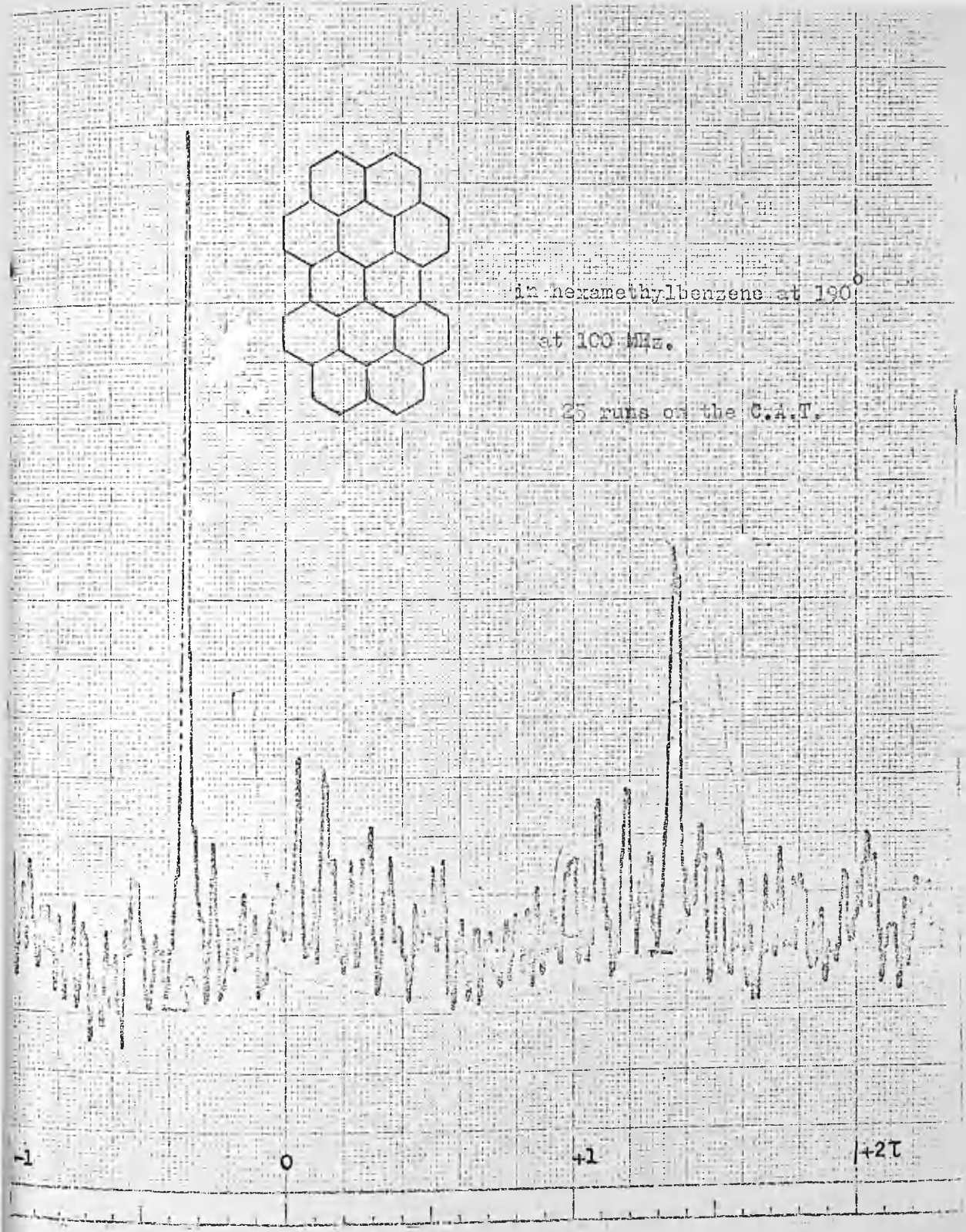
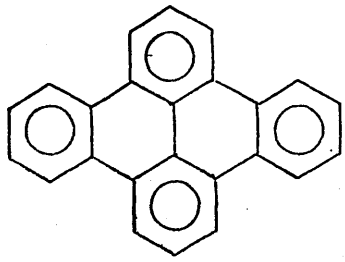
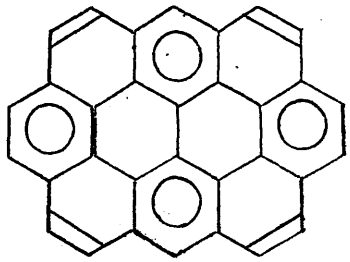

in hexamethylbenzene at 190°
at 100 MHz.
25 runs on the C.A.T.
-1
0
+1
+2τ

Fig 3a

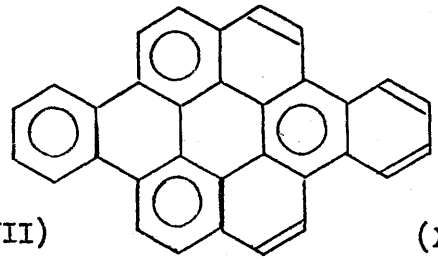


(XXV)

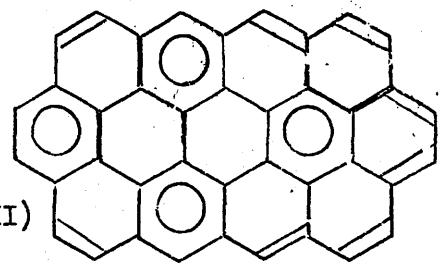


(XXVI)

λ_β = 2880 $\xrightarrow{+610}$ 3490 Å

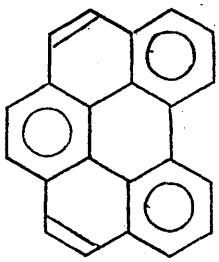


(XXVII)

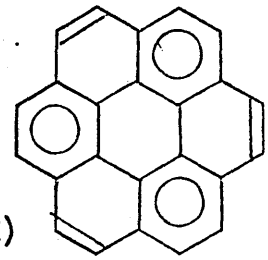


(XXVIII)

λ_β = 3300 $\xrightarrow{+700}$ 4000 Å



(XXII)



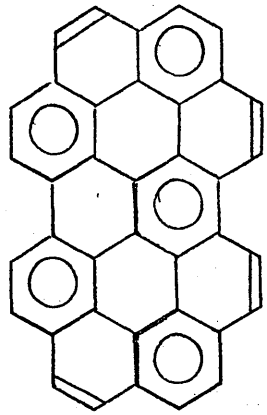
(XXIII)

λ_β = 3030 $\xrightarrow{+20}$ 3050 Å

highly condensed hydrocarbons. Thus it is of interest to try and predict the bands of a new hydrocarbon and compare them with the observed bands. The addition of three ethylene bridges to triphenylene (XXIV) forming coronene (XXIII) gives a β-band shift to the red of 480Å. Similarly addition of four ethylene bridges to 1,2:6,7-dibenzopyrene (XXV) forms ovalene (XXVI) with a corresponding shift of the β-band by 610Å, and four bridges to 1,2:7,8-dibenzocoronene (XXVII) gives circumanthracene (XXVIII) with a shift of 700Å. Hence one can consider an increment of approximately 160Å per ethylene bridge if the effect is linearly additive for each successive bridge. If one adds four ethylene bridges to 1,12:2,3:10,11-tribenzo - perylene (XXIX) forming circobiphenyl, the β-band shift should be of the order of 640Å resulting in a new β-band at 3640Å, which is in fact close to the observed band at 3630Å.

However the addition of ethylene bridges has to be used with caution as can be seen from the addition of two bridges to 1,12:2,3:10,11-tribenzoperylene (XXIX) at different positions. If addition takes place at the 4,4' and 9,1" positions, 3,4:5,6: 7,8-tribenzoperopyrene (XXX) is formed, and the expected shift of 320Å agrees well with the new β-band found at 3310Å. A further addition of two bridges gives circobiphenyl with a further shift of 320Å giving the observed band at 3630Å.

However a very different situation arises when the ethylene bridges are added at the 1' , 1" and 2' , 4" position of

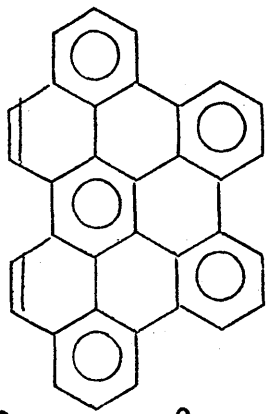


(XVI)

$\lambda\beta$ = 3630 Å

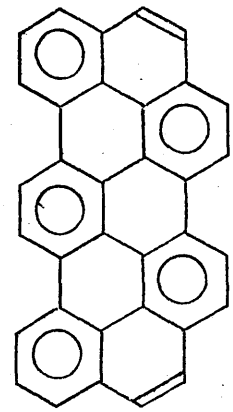
+ 70

+ 320



(XXXI)

$\lambda\beta$ = 3580 Å

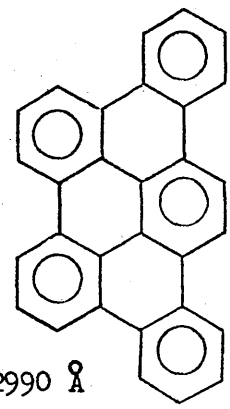


(XXX)

$\lambda\beta$ = 3310 Å

+ 580

+ 320



$\lambda\beta$ = 2990 Å

(XXIX)

1,12:2,3:10,11-tribenzoperylene (XXIX). The new β-band of the formed 3,4:11,12-dibenzobisanthene (XXXI) is at 3580Å, with a red shift of 580Å almost double the effect previously observed. Addition of a further two ethylene bridges to give circobiphenyl only requires a shift of 50Å for the observed band at 3630Å. This is a very asymmetric effect and can be compared directly with the effect of addition of an ethylene bridge to 1,12-benzoperylene (XXII) giving coronene (XXIII). This is accompanied by a shift of the β-band of only 20Å.

Therefore 3,4:11,12-dibenzobisanthene (XXXI) must have an electronic arrangement in the two halves of the molecule which is very similar to that of 1,12-benzoperylene, as they are both little affected by the addition of ethylene bridges. This cannot be the case for 3,4:5,6:7,8-tribenzoperopyrene (XXIX) which shows very different electronic shifts when two ethylene bridges are added to the molecule. In fact this structure can only really be considered a peropyrene derivative by virtue of its arrangement of rings, as with five sextets drawn, it never attains an electronic arrangement like that of peropyrene (structure XXX). On the other hand 3,4.11,12-dibenzobisanthene (XXXI) is better considered a derivative of peropyrene as it readily adopts a peropyrene electronic arrangement (XXXI) as shown, when the structure is assigned five sextets. This would account well for the observed differences in the electronic spectra of these two molecules.

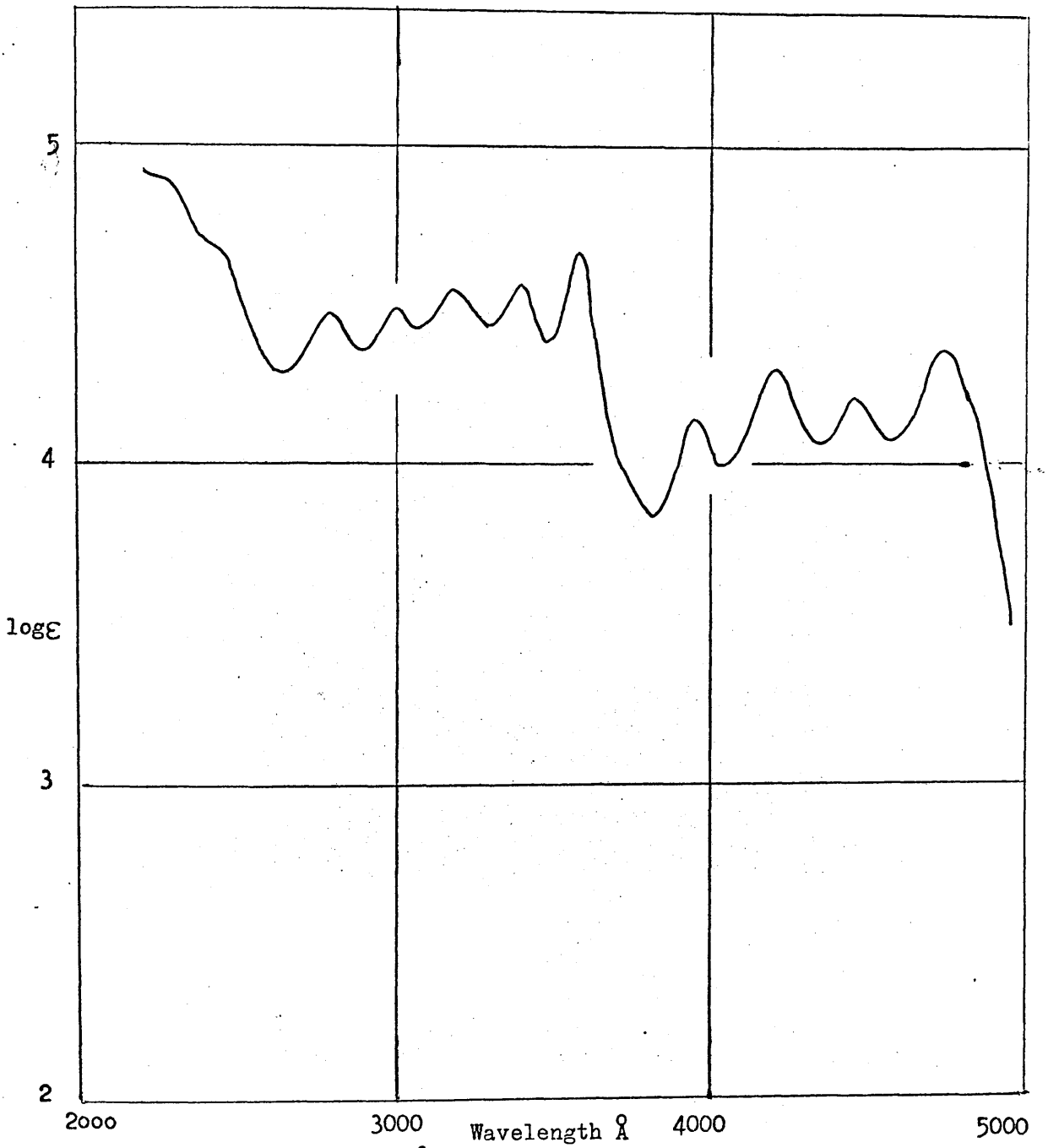


Fig. 6 Absorption max (Å) and log ε (in parentheses)
Red hydrocarbon ($C_{38}H_{20}$) in cyclohexane ρ: 4760(4.37), 4465(4.21), 4215(4.30), 3980(4.15); β : 3580(4.67), 3400(4.57), 3180(4.55), 2995(4.50), 2775 (4.48).

Finally the fifth dimeric compound isolated from the zinc dust reaction was a bright red hydrocarbon which was readily recrystallised from cyclohexane. This was much more soluble and had a lower melting point than the other compounds obtained. The analysis and mass spectrum favour a molecular formula of $C_{38}H_{20}$ and it was assigned the structure (XLIV) on the basis of its U.V. spectrum which was similar to 1,14:3,4:7,8:10,11 - tetrabenzoperylene[11] (XIV). However the n.m.r. spectra although indicating two methylene protons at 6.55τ did not give a sharp singlet at low field which one would expect from the bay protons of this structure (XLIV). The spectra is in fact very complex and points to an asymmetric compound. The possibility of a mixture was discounted on the grounds that the relative intensity of the ρ-bands were unaltered after chromatography or recrystallisation, however its structure remains unsolved.

Experimental Discussion

The general method already mentioned of dimersing perinaphthone[2] and benzanthrone[15] to the corresponding peropyrene and dibenzoperopyrenes was applied to 6- naphthanthrone(XXXII). 6 - Naphthanthrone was prepared by an improved method and underwent bimolecular condensation when heated with zinc dust and a few drops of water in a sealed tube. The U.V. spectrum of the resulting mixture indicated the presence of a number of compounds and subsequent extraction with light petrol and xylene, chromatography of these concentrated solutions and sublimation of the organic residue left after extraction, resulted in the isolation of seven compounds, two monomeric and five dimeric derivatives of naphthanthrene.

The two monomers were naphthanthrene[16] (XXXIIIfound in traces) and trimethylenepyrene[17] (XXXIV) which are reduction products of 6 - naphthanthrone. The normal reductive process will be occuring along with bimolecular condensation, although with small amounts of water, the source of hydrogen is restricted and this process is minimised. The two compounds were readily identified by their U.V. spectra. Fig. 4

Two of the higher derivatives were known compounds. Dinaphtho - (7,1':1,2);(1",7";6,8) - peropyrene (IX) had already been unambiguously synthesised[9] and was also present as the main component from a zinc chloride, zinc dust melt of 6 - naphthanthrone.[7] The other known peropyrene derivative also isolated from the above melt has been assigned the structure (X), although it is not certain if this structure is the correct one.[7] Their U.V. spectra are shown in Fig. 5.

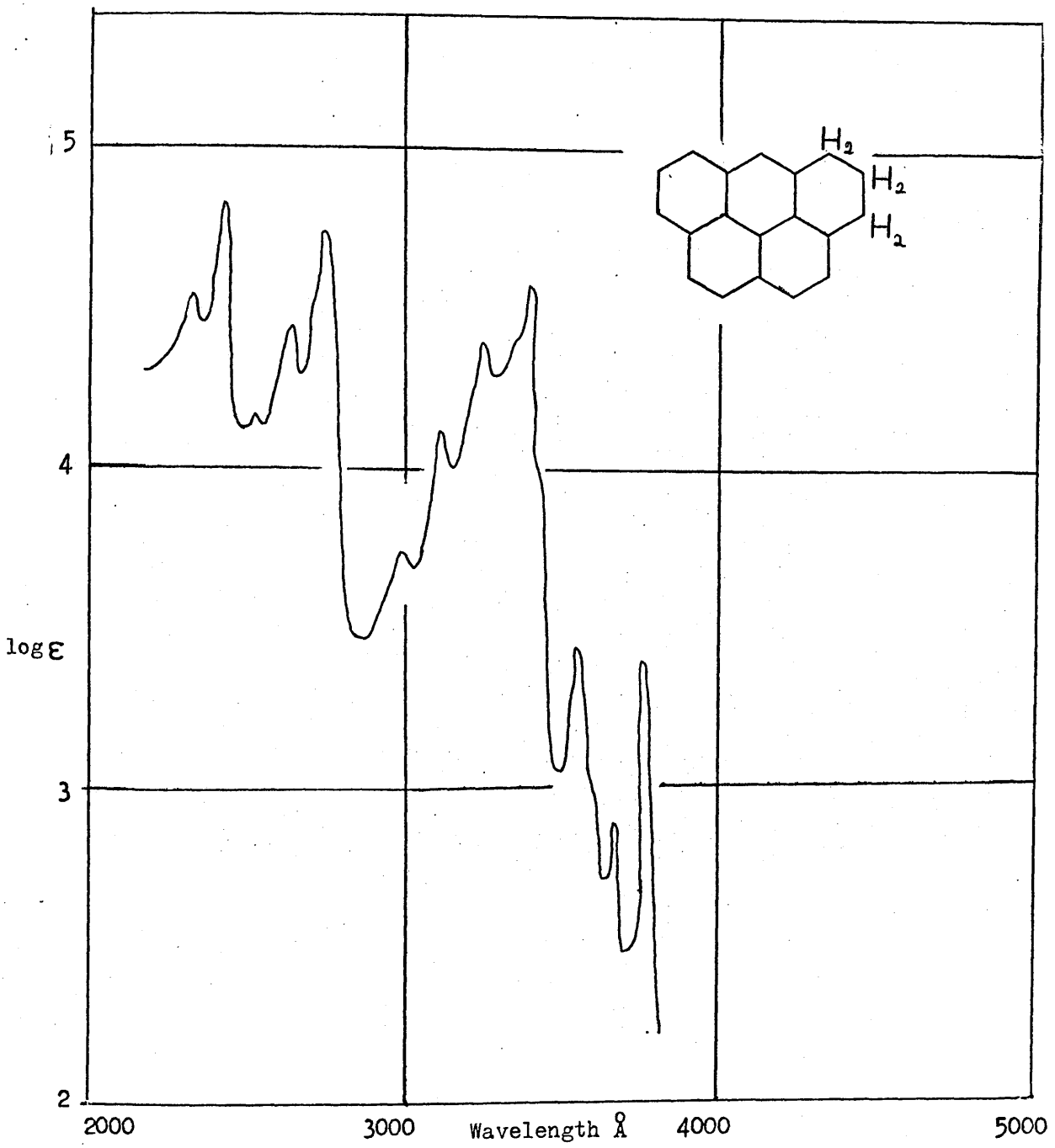


Fig. 4 Absorption max (Å) and log ε (in parentheses)
Trimethylenepyrene in alcohol, α : 3780(3.40), 3700(2.87), 3575(3.44); ρ : 3430(4.57), 3270(4.40), 3130(4.12), 3010(3.75); β : 2770(4.74), 2550(4.18); β′ : 2445(4.84), 2345(4.55).

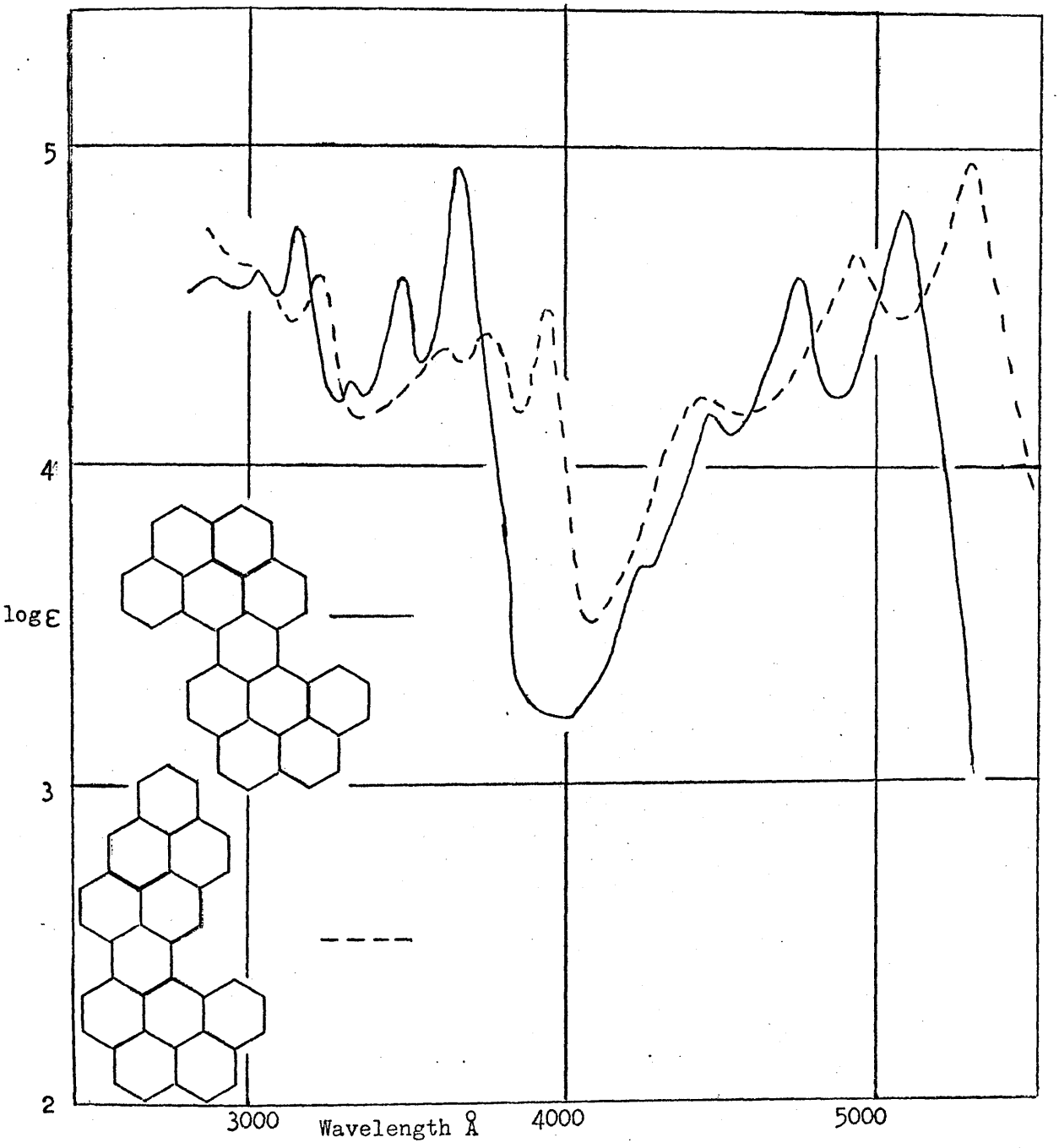


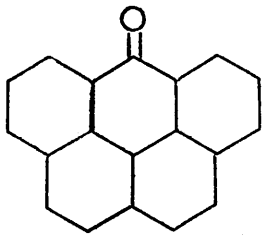
Fig. 5 Absorption max (Å) and log ε (in parentheses)

—— Dinaphtho - (7',1':1,13); (1",7":6,8)- peropyrene in benzene

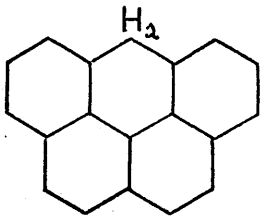
ρ: 5100(4.80), 4760(4.59), 4470(4.16); β : 3670(4.92), 3490(4.58), 3340(4.26); β′ ; 3170(4.72), 3040(4.61).

---- Dinaphtho - (7',1':1,13);(1",7":9,11) - peropyrene in xylene

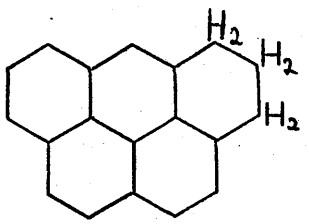
ρ: 5325(4.93), 4950(4.65), 4650(4.20); β : 3950(4.49), 3755(4.42), 3625(4.37); β′ : 3240(4.65).



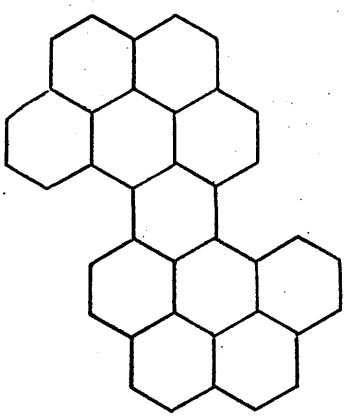
(XXXII)



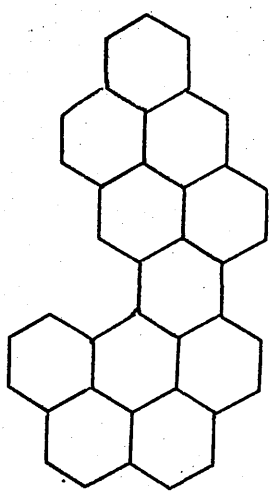
(XXXIII)



(XXXIV)



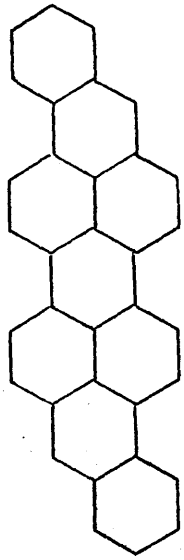
(IX)



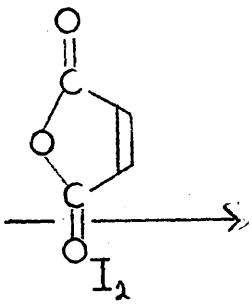
(X)

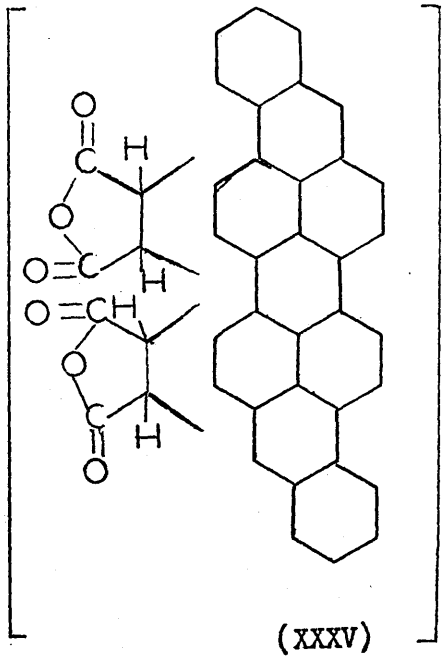
The new hydrocarbon, circobiphenyl, was obtained in a pure state by subliming the hydrocarbon residue left after extraction with light petrol and xylene, and dissolving the zinc dust in conc. hydrochloric acid. It was also recrystallised from 1 - methyl-naphthalene as pale yellow - green needles. Circobiphenyl being a fully condensed hydrocarbon has therefore undergone a further condensation, after the initial dimerisation, involving the loss of two more hydrogen atoms. It therefore has the formula $C_{38}H_{16}$ which was confirmed by microanalysis and from examination of the mass spectrum.

Another new hydrocarbon, assigned the structure (XIII) on the basis of its U.V. spectrum, was present in the mixture in fair proportions, however only a small amount was obtained in a pure state as it proved extremely difficult to separate from the isomer(X). The mass spectrum and microanalysis confirm that it has the formula $C_{38}H_{18}$. As mentioned already it readily reacts with maleic anhydride twice forming a purple tetracarboxylic adduct which can be converted to the corresponding dianhydride by refluxing with acetic anhydride this is shown by the analysis figures and the structures (XVa,bc) cannot be excluded. Attempts to dehydrogenate this adduct with iodine or chloranil were completely unsuccessful, as were decarboxylation attempts which merely resulted in dissociation of the adduct. As expected none of the other isomers isolated reacted with maleic anhydride even after prolonged refluxing with the addition of dehydrogenating agents such as chloranil or iodine.

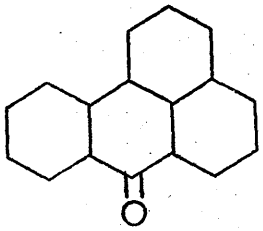


(IIa)

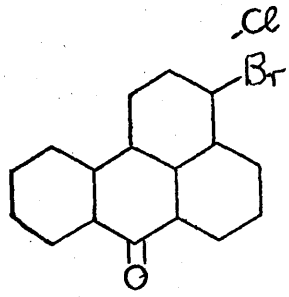




(XXXV)



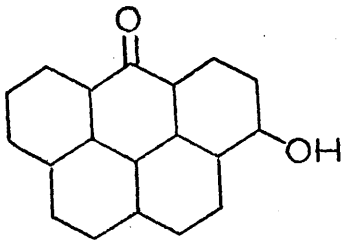
(XXXVI)



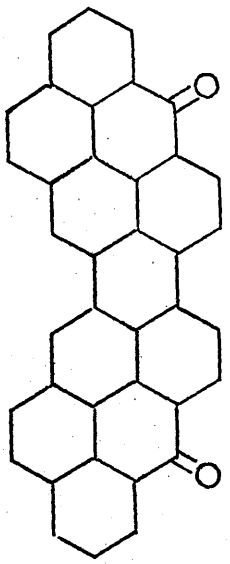
(XXXVII)

Isoviolanthrene (IIa) and violanthrene (IIb) were also refluxed with maleic anhydride and no trace of an adduct could be detected in the case of the latter hydrocarbon. However prolonged treatment of isoviolanthrene (IIa), with addition of a crystal of iodine, and subsequent extraction of the mixture with dil. alcoholic alkali gave a weakly coloured solution with ρ-bands at 5300, 4910, 4600 and β-bands at 3600 and 3440Å.. Acidification of the extract gave a small amount of reddish-brown precipitate(XXXV) >1mg. which was collected by centrifuging. However the analysis results did not fit any plausible structure being too low in carbon. A better spectrum of this adduct was obtained in diethylenetriamine with shifts of the ρ-band from 5180 to 5290 Å and the β-band from 3560 to 3600 Å in direct comparison with the spectrum of the hydrocarbon also in diethylenetriamine. There is very little change in the overall shape of the two spectra apart from this shift to longer wavelengths. However it must be emphasised that only a very small amount of this adduct was obtained, the vast majority of the hydrocarbon remaining unaltered, even when the quantities of starting material were increased.

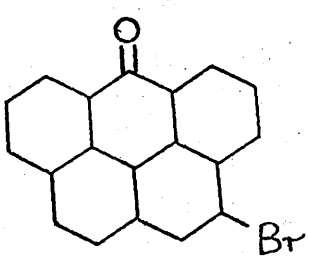
In a classical paper dealing with the reactions of benzanthrone (XXXVI), Lüttringhaus and Neresheimer[18] showed that isoviolanthrone and violanthrone were formed when benzanthrone was heated with alcoholic potassium hydroxide and that the yields of the isomers were dependent on the reaction temperature. Isoviolanthrone could also be synthesised specifically by heating either 3-chloro or



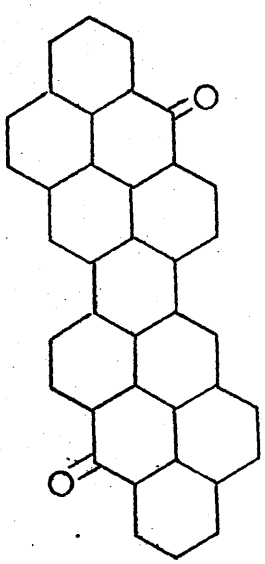
(XXVIII)



(XXXIX)



(XL)



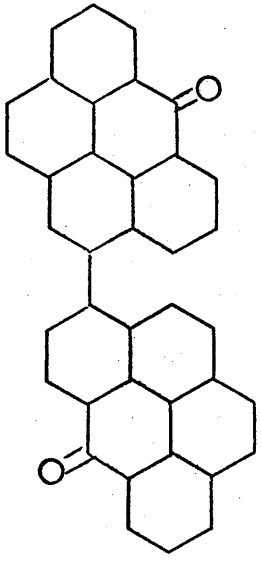
(XLI)

3 - bromobenzanthrone (XXXVII) with alcoholic potassium hydroxide as this process does not give the other isomer.

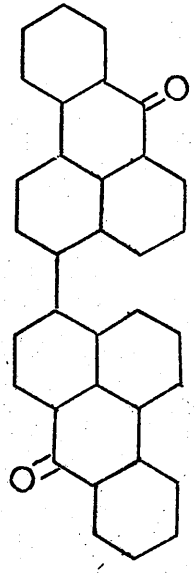
A more recent study[19] has shown that this procedure is not as readily applied to 6 - naphthanthrone. When this compound is heated with alcoholic potassium hydroxide at 110° and with the temperature as high as 125°, 6 - naphthanthrone remains unchanged. a more rigorous treatment at 250° using a melt of potassium hydroxide and potassium acetate gave mono-hydroxy derivative, assumed to be 3-hydroxy-6-naphthanthrone (XXXVIII), and a dark blue quinoid diketone[16] which was assigned the structure of dibenzoviolanthrone (XXXIX) in analogy with Lüttringhaus and Neresheimer work.[18]

A monobromo-6-naphthanthrone was also formed[19] by reacting equimolar quantities of bromine and 6-naphthanthrone and this was thought to be 2-bromo-6-naphthanthrone (XL) in view of the fact that it formed a dark blue quinoid diketone when treated with alcoholic potassium hydroxide at 115°, the conditions used for fusion of 2-bromobenzanthrone to isoviolanthrone. It was therefore assigned the structure of the dibenzisoviolanthrone (XLI) again in analogy with the earlier work.[18]

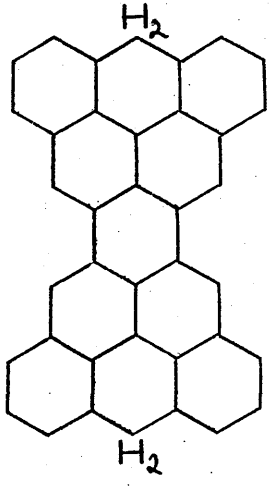
In view of the uncertainty of the position of the bromine in this monobromo derivative and the rather lengthy purification procedure,[19] this approach was not pursued. Instead 6-naphthanthrone was refluxed for several days with potassium hydroxide, xylene and isopropanol and gave a brown resinous mixture. The U.V. spectrum showed mainly unreacted 6-naphthanthrone. However sublimation of this solid material gave, along with a black tar, a 50/50 mixture



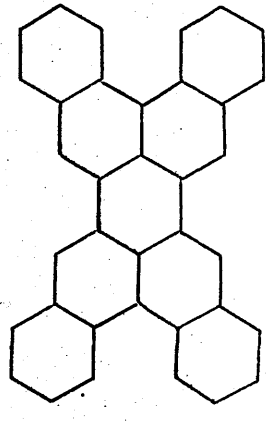
(XLII)



(XLIII)



(XLIV)



(XIV)

of isomers (XIII) and (X). There was no trace from U.V. spectra of (IX) or any of the other isomers previously obtained from the zinc dust treatment. If the naphthanthronyl (XLII) intermediate, similar to the dibenzanthronyl (XLIII) derivative obtained by this process from benzanthrone, was present, it is difficult to explain why mere sublimation produced the final hydrocarbons. On the otherhand if bimolecular condensation has been occuring it is unlikely that none of the other isomers especially (IX) have been formed. If the intermediate (XLII) was formed it would add evidence to the fact that compounds (XIII) and (X) were in fact the isomeric dibenzviolanthrenes however no trace of (XLII) could be detected, although a T.L.C. plate of the crude alkali melt reaction mixture showed at least twenty spots.

A potassium hydroxide, potassium acetate melt of 6-naphthanthrone at 250° was repeated exactly as described by Bradley and Sutcliffe, but with a longer reaction time of 3 hours; 3-hydroxy-6-naphthanthrone and a small quantity of black residue were formed.

Instead of the lengthy purification process undertaken by the above authors[19] to obtain the quinone in a pure state, the solid was thoroughly extracted with trichlorobenzene, filtered and the solution taken to dryness. A direct zinc chloride, sodium chloride, zinc dust melt gave a product which dissolved in trichlorobenzene indicating a mixture of all the four isomer (IX),(X),(XVI), (XIII) previously obtained. This unfortunately did not produce a single pure compound as hoped and further work was discontinued.

EXPERIMENTAL

6-Naphthanthrone (VIIIa).

Naphthanthrone was prepared by the improved method of Ironside and was obtained as light brown prisms from ethanol m.pt. 241-243° (Lit. m.pt. 243°).[20]

Zinc dust condensation of 6-Naphthanthrone.

6-Naphthanthrone (3 gm.) was powdered intimately with zinc dust (15 gm.) and heated with 2-3 drops of water in a sealed tube at 310° for 50 hours. The dark red-purple solid mixture from four such tubes was broken up and finely powdered. The U.V. spectra of solutions of the crude product indicated a mixture of several hydrocarbons and an initial separation was effected by extracting the powdered solid with light petroleum (100-120°) and xylene and subsequent chromatographing of these solutions.

Chromatograph of the light petrol extract.

The above powdered solid was thoroughly extracted with three litres of boiling light petroleum (100-120°), the solution filtered and the insoluble residue retained. The petrol solution was dried with anhydrous sodium sulphate, concentrated and chromatographed over Grade I neutral alumina.

Eluting with light petroleum (100-120°) gave a colourless solution with a blue fluorescence which on concentration yielded pale yellow leaflets of trimethylenepyrene identified by the U.V. spectrum. Further elution with benzene gave an orange-yellow band which contained a number of compounds and this solution was retained for rechromatographing (Solution A).

Chromatograph of the xylene extract.

The above residue was again thoroughly extracted, this time with four litres of boiling xylene, filtered and the insoluble residue retained.

The solution was concentrated to 800 ml. and on standing overnight yielded a dark reddish-purple crystalline deposit which was filtered and dried (1.8 gm.). The solution was further concentrated to 150 mls. and prior to chromatographing a further precipitate was filtered off and dried (2.5 gm.).

The remaining reddish-brown solution was chromatographed over Grade I neutral alumina. Elution with cyclohexane gave a colourless solution with a blue fluorescence which yielded a further quantity of trimethylenepyrene. A yellow-orange band followed which contained a mixture of hydrocarbons similar to that obtained from the first chromatograph and these fractions were bulked and this solution, A', was retained.

Further elution with benzene/xylene (50/50) gave and orange-red band with a green fluorescence which was completely developed with xylene. Concentration of these fractions yielded orange red needles of the known dinaphtho-(7'.1':1.13); (1",7":6,8)-peropyrene (IX) (1800 mg). Development of the column with boiling xylene produced a mixture of two more hydrocarbons which on U.V. examination proved to be the known dinaphtho-(7'.1';1.13); 1".7":9.11)-peropyrene (X) and a new hydrocarbon. The fractions enriched in the latter hydrocarbon gave rose-red solutions with an orange fluorescence and concentration of these gave a small amount (2 mg.) of dark purple needles. The last fractions from the column were reddish brown solutions with a green fluorescence and concentration of these gave almost pure dinaphtho-(7'.1': 1.13); (1".7":9.11)-peropyrene (26 mg.) (X). Further eluting with boiling trichlorobenzene gave only very weak solutions of the hydrocarbon (X).

Rechromatograph of the combined solutions A and A'

The orange-yellow solutions A and A' of the mixture of hydrocarbons which were not separated on the first two columns were combined and rechromatographed over Grade I neutral alumina. Graded elution with various proportions of cyclohexane/benzene gave a further quantity of trimethylenepyrene, traces of naphthanthrene recognised from the U.V. spectrum, a further

quantity of orange red needles of dinaphtho-(7'.1':1.13); (1".7": 6.8)-peropyrene (150 mgs.), and bright scarlet platelets of a new hydrocarbon (50 mgs.). This new hydrocarbon was recrystallised from cyclohexane as thin bright scarlet prisms, m.pt. 277-279° (dec.), M.S. molecular ion $^{m}/_{e}$=476; calculated M.W.=476 for $C_{38}H_{20}$. The hydrocarbon dissolved slowly in concentrated sulphuric acid forming a greenish-blue solution. The U.V. spectrum is shown in Fig. 6.

Found		C=95.17%, H=4.75%
		C=95.30%. H=4.77%
$C_{38}H_{20}$	requires	C=95.80%, H=4.20%

Isolation and purification of Circobiphenyl (XVI).

The residue left after extraction of the crude reaction product with light petrol and xylene was boiled with concentrated hydrochloric acid for several hours to destroy the zinc dust. The remaining organic product was filtered, washed with dilute ammonia and water and dried (6.2 gm.). The U.V. spectrum of this product in trichlorobenzene indicated the presence of the two dinaphthoperopyrenes (IX,X) already isolated and the new purple hydrocarbon (XIII).

However a considerable amount of product was only sparingly soluble and the mixture was therefore sublimed. At 310°,

(10^{-4} m.m. Hg.), dinaphtho-(7'.1':1.13);(1".7":9.11)-peropyrene (IX) sublimed and up to 400° the other two hydrocarbons (X) and (XIII)sublimed off together. Temperatures in excess of 400° yielded bright olive blades of a hitherto undetected hydrocarbon. This extremely insoluble compound could easily be isolated almost in a pure state merely by refluxing the sublimate in boiling xylene which dissolved other hydrocarbon impurities. Recrystallisation was possible using boiling redistilled 1-methylnaphthalene, the hydrocarbon crystallising from the almost boiling brown yellow solution as fine bright yellow-green needles, m.pt. 480-483°, M.S. molecular ion $^{m}/_{e}$ 472; calculated M.W.= 472 for $C_{38}H_{16}$. The hydrocarbon dissolves slowly in warmed concentrated sulphuric acid forming a reddish-brown solution. The U.V. spectrum is shown in Fig. 3.

Found		C=96.32%, H=3.63%
$C_{38}H_{16}$	requires	C=96.59%, H=3.41%

Attempted separation of hydrocarbons (IX, X and XIII) by high vacuum sublimation.

The U.V. spectrum of a solution of the purple-red crystalline product which had precipitated on concentration of the xylene extract prior to chromatography (4.3 gms.) indicated a mixture of three hydrocarbons. The major constituent was dinaphtho-(7'.1':1.13); (1".7":6.8)-peropyrene (IX) which could almost be completely separated from the mixture by sublimation with

a maximum temperature of 330° (10^{-4} m.m. Hg.).

The residue from this sublimation was then completely sublimed yielding a further small amount of (IX) and at temperatures in excess of 350°, two overlapping bands consisting of (X) and(XIII) sublimed off together.. These two hydrocarbons could not be separated from each other by this method even with long sublimation times (3 hours) and gradual increases in temperature, but were completely separated from (X) and a sample (45 mgs.) was obtained. However recrystallisation of this mixture from mesitylene furnished a quantity (12 mgs.) of the purple hydrocarbon (XIII) in an almost pure state. m.pt. 427-430°, which dissolved in concentrated sulphuric acid on warming with a violet colour. M.S. molecular ion $^{m}/_{e}$ 474: calculated M.W. = 474 for $C_{38}H_{18}$.

Found		C=96.11%, H=3.84%
$C_{38}H_{18}$	requires	C=96.18%, H=3.82%

Addition of maleic anhydride to hydrocarbon (XIII).

A mixture (5.2 gm.) of the three hydrocarbons (IX,X and XIII) was refluxed for twenty minutes with 30 gm. of purified maleic anhydride. The purple-red solution darkened only slightly and was poured into water and the residue thoroughly washed

with hot water to remove excess maleic anhydride. The residue was extracted overnight with dilute sodium hydroxide solution containing 50% alcohol and the purple mixture cooled and filtered. The residue was washed with water and dried (4.4 gms.), U.V. examination showed that almost all the hydrocarbon (XIII) had reacted leaving (IX) and(X) as the residue.

The clear deep purple solution was filtered and carefully acidified with concentrated hydrochloric acid and the very fine purple precipitate allowed to settle. Separation of this precipitate from the mother liquor proved impossible by normal suction or gravity filtration methods, and centrifuging was used. The colourless mother liquor was decanted after each centrifugation and replaced with distilled water thus washing the precipitate acid free. Finally the precipitate was dried giving a dark purple brittle solid (500 mg.) m.pt. $> 500^{\circ}$ which dissolved slowly in concentrated sulphuric acid forming an olive green solution.

Found	C=78.91%, H=3.86%
$C_{46}H_{26}O_{8}$ requires	C=78.19%, H=3.68%
$C_{46}H_{22}O_{8}$ requires	C=78.63%, H= 3.13%

Formation of the anhydride from the tetracarboxylic acid derivative

The above tetracarboxylic acid (10 mgs.) was finely powdered and refluxed for 40 mins. with excess acetic anhydride (3 mls.) giving a deep purple solution, although not all of the product dissolved. The cooled mixture was filtered, thoroughly washed with benzene and dried under vacuum.

Yield 8 mgs. m.pt. $> 500^{\circ}$

Found		C=82.34%, H=3.44%
$C_{46}H_{22}O_6$	requires	C=82.40%, H=3.29%
$C_{46}H_{18}O_6$	requires	C=82.88%, H=2.70%

Attempted dehydrogenation of the anhydride (XVb)

The above anhydride (6 mg) was refluxed for one hour with acetic anhydride (3 mls.) and a crystal of iodine. The brown solution was cooled and the dark purple powder filtered, washed with acetic anhydride and benzene and dried(5mg). A pale green fringe was observed at the liquid surface level of the flask and the U.V. spectrum in trichlorobenzene showed bands at 8140 and 7500 $\overset{\circ}{A}$ which were very weak due to the poor solubility of the product.

Found		C=81.64%, H 3.15%
$C_{46}H_{14}O_6$	(fully aromatic) requires	C=83.38%, H=2.11%

Attempted decarboxylation of the tetracarboxylic acid adduct (XVa)

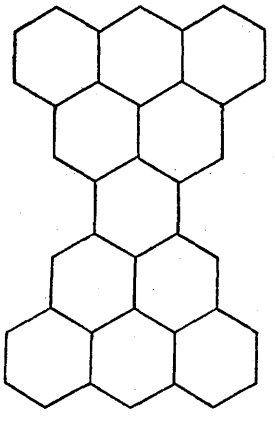
The tetracarboxylic acid (50 mgs.) was sublimed slowly for several hours under good vacuum. At 200° (10^{-4} m.m. Hg.) a pale yellow non-crystalline product sublimed. The temperature was slowly raised to 380° and a purple product started to sublime. The temperature was held at 380-410° for two hours. The tube was cooled, the sublimation boat removed and the residue weighed (38 mgs.). The purple sublimate was scraped from the tube, extracted with a small amount of dil. alcoholic sodium hydroxide, recrystallised from xylene and dried. (2 mgs.). The U.V. spectrum was almost identical to that of the pure hydrocarbon (XIII).

Found C=92.92%, H=3.93%

$C_{38}H_{18}$ requires C=96.18%, H=3.82%

CHAPTER 4.

ATTEMPTED SYNTHESIS of 1,14:3,4:7,8:10,11-TETRABENZOPEROPYRENE



(I)

INTRODUCTION

The theoretical uncertainty of the stability of this hydrocarbon prompted an attempt to synthesise the basic carbon skeleton unambiguously, in an analogous manner to the successful route developed for synthesis of triangulene derivatives. It was also hoped that synthesis of (I) would clarify the apparently anomolous addition of maleic anhydride to the purple hydrocarbon discussed in the previous chapter.

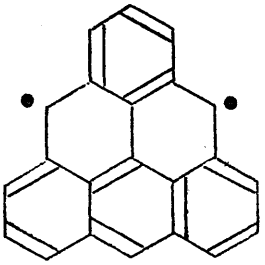
Discussion

Several definitions of the electronic requirements for the existence of a benzenoid hydrocarbon as a stable molecule have been put forward in the light of the various theoretical approaches.

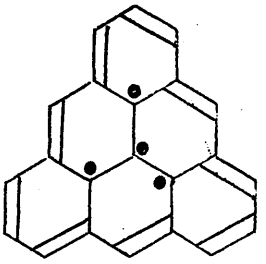
The Valence Bond Theory requires that the molecule must have two or more Kekulé structure each of which contributes towards the normal state of the molecule to a certain fixed percentage, depending on its stability.[1] From this definition a structure with none or only one Kekulé structure is not considered capable of existence as a stable aromatic hydrocarbon.

In the quantum mechanical approach the π-electrons are considered to be distributed over the whole ring system, in pairs, in the lowest energy molecular orbitals.[2] This method does not require that a stable aromatic system should be capable of being written in a classical form with one or more Kekulé structures.

Thus in order to find out how these considerations are relevant, it is of considerable interest to try and synthesise aromatic hydrocarbons which can be written with only one or with no Kekulé structures. The latter case is exemplified by the structure (I) with the composition $C_{22}H_{12}$, which is the hydrocarbon triangulene. This cannot be formulated in any way with Kekulé structures and therefore can only be written according to classical structural theory as a diradical.



(I)



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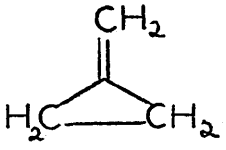

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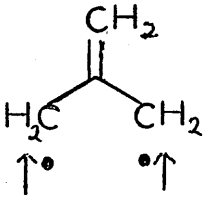

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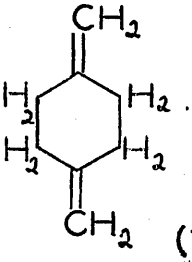

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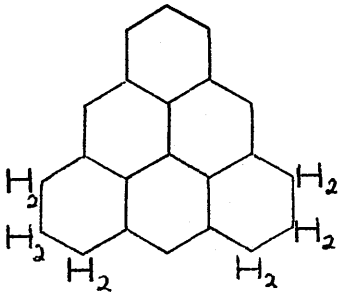
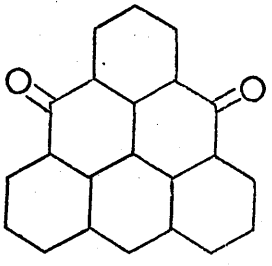


(VI)



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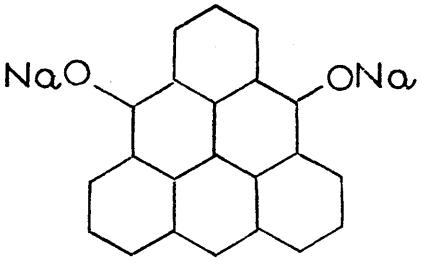
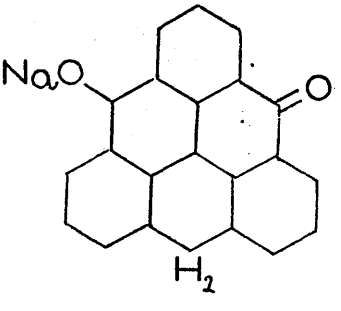


(VIII)



(IX)

This was first postulated by Clar from this standpoint[3] and confirmed soon after by Longuett-Higgins, whose molecular orbital calculations showed that the triangulene structure would indeed exist as a diradical.[4]

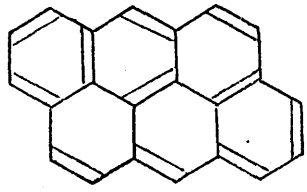
The structure (II) can also be considered as a polyenic framework with the internal four π-electrons (indicated by dots) capable of being arranged in two orbitals, but not in double bonds. If the four carbon atoms in the centre of triangulene are removed, the remaining annulene system has two Kekule structures and is stable. These four internal carbon atoms can exist in the stable methylenecyclopropane arrangement (III), but this would require the formation of a bond between meta carbon atoms if it were replaced in the triangulene structure, and todate, there are no polycyclic aromatic hydrocarbons with this form of bonding.[5] The other possible arrangement is trimethylenemethane (IV) which has two free valencies. This has been isolated and shown to exist in the triplet ground state, the two electrons having parallel spins. Two such molecules with opposed sets of spins can dimerise to form 1,5-dimethylenecyclohexane (V), but intra-molecular cyclisation of an individual trimethylenemethane molecule to form methylenecyclopropane is not allowed, as the bond would have electrons with parallel spins.[6] This structure is therefore more related to the centre of triangulene as opposed

to structure (III) which has a meta carbon bond.

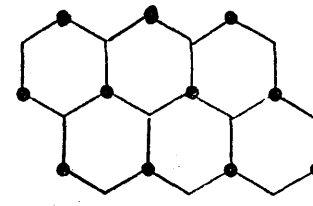
The experimental evidence shows without doubt that triangulene is a diradical and not a stable aromatic hydrocarbon.[7] Dehydrogenation of the stable hexahydrotriangulene (VI) using palladium charcoal at 300°, conditions which are mild enough for dehydrogenation to the most sensitive hydrocarbons, results in a polymer which could not be sublimed from the catalyst even under vacuum, at high temperature. A brown polymer was also formed when dehydrogenation was attempted using palladium charcoal in trichlorobenzene at 200°.[7]

Further experimental proof of the instability of the triangulene skeleton, at even lower temperatures, is evident from attempts to reduce the stable red triangulenequinone (VII).[7] It should not show the properties of a normal quinone, as the two carbonyls have to be reduced independently to avoid the triangulene structure (VIII), which would result if normal quinone reduction was occurring. In fact treatment of triangulenequinone with alkaline sodium dithionite does give a green solution but this is due to the formation of the mono-sodium salt (IX), readily shown by analysis. Hence even at temperatures of less than 100° the triangulene skeleton is not stable and the molecule favours the alternative arrangement as in (IX).[7]

The yellow hydrocarbon anthanthrene (X) is isomeric with triangulene but has a different annellation of three carbon



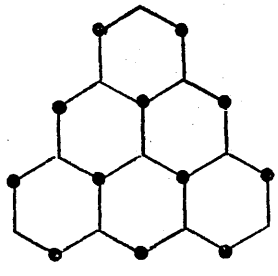
(X)



(XI)

Marked atoms = 11

Unmarked atoms = 11

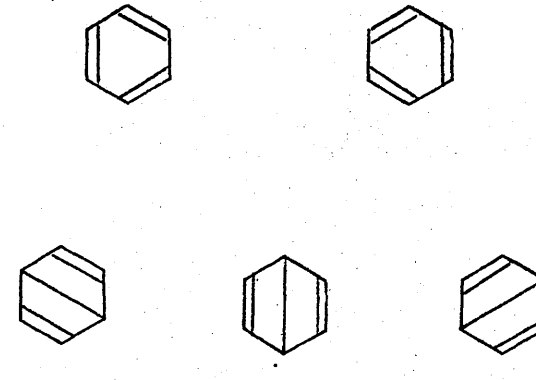


(XII)

Marked atoms = 12

Unmarked atoms = 10

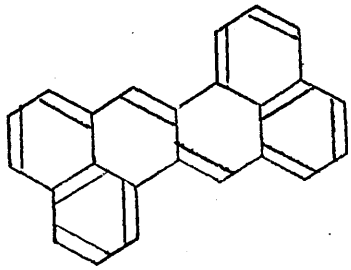
(XIII)



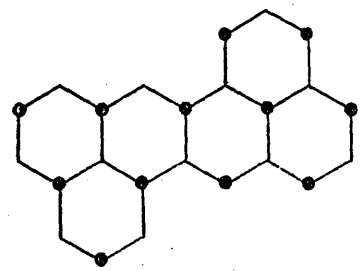
atoms of one ring. Anthanthrene can be written with several Kekulé structures and is a stable aromatic hydrocarbon. This difference in stability between the two isomeric hydrocarbons can be readily demonstrated in another way.

If one marks the alternant carbon atoms of anthanthrene (XI), as shown, then there are the same number of marked as unmarked carbon atoms.[8] The marked carbon atoms can be considered as having π-electrons of the same spin, while the unmarked atoms have electrons of the opposite spin. Hence π-electron pairs can be formed in many ways from electrons originating from ortho and para carbon atoms, but a meta bond is ruled out as this would involve pairing of two π-electrons with parallel spins in violation of the Pauli principle.[9] Therefore the impossibility of meta bonding in polycyclic aromatic hydrocarbons is inherent in this scheme.

Formula (XII) shows the alternant marking for triangulene and there are two more marked than unmarked atoms. This means that there are two π-electrons with parallel spins which cannot be paired and the molecule must exist as a diradical. This method was first introduced by O.Schmidt[10] and V.A.Izmail'ski.[11] The latter author showed that the structures of the valence bond method are inherent in the marked benzene ring and if one writes bonds between marked and unmarked carbon atoms in benzene, the two Kekulé structures and the three Dewar structures



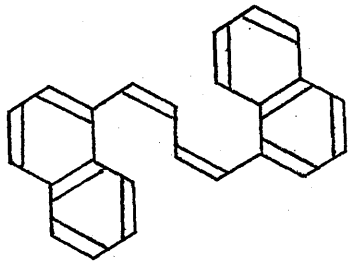
(XIV)



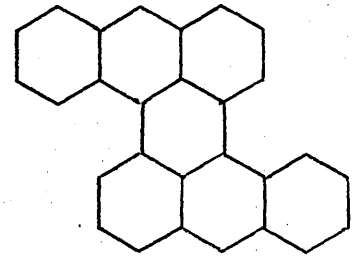
(XV)

Marked atoms = 12

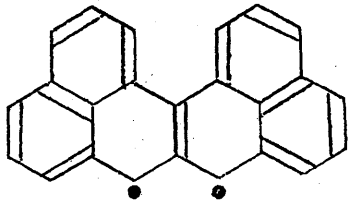
Unmarked atoms = 12



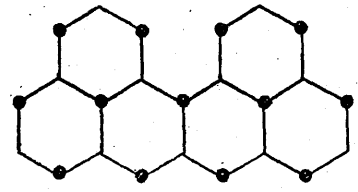
(XVI)



(XVIa)



(XVIII)



(XVII)

Marked atoms = 13

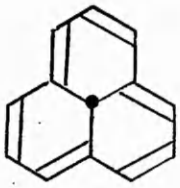
Unmarked atoms = 11

are obtained (XIII).

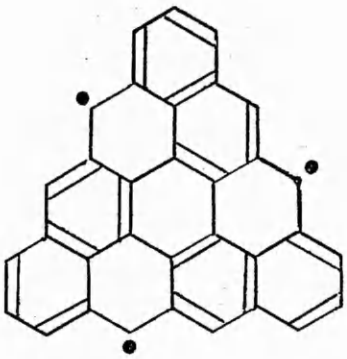
This method also satisfactorily explains the stable existance of the zethrenes despite the fact that they can only be written with one Kekulé structure.[12] The formulation of zethrene with double bonds (XIV) also contains two naphthalene complexes each of which can be written with three Kekulé structures. Nevertheless, the two central bonds remain fixed, and if mobility of all the double bonds is considered a criterion for aromaticity, then zethrene cannot be an aromatic hydrocarbon.[12]

However the alternant marking shows (XV) that there is an equal number of marked and unmarked carbon atoms (12 and 12) and therefore this theory predicts that zethrene will be stable. The absorption spectrum of the red zethrene shows all the characteristics of an aromatic hydrocarbon and is quite similar to the spectrum of 1,2:7,8-dibenzoperylene (XVIa), which does not have fixed double bonds.[13] Di-2-naphthylbutadiene (XVI) on the other hand, which has the same fixed double bonds as zethrene, but not in hexagons, has a spectrum which is very different from that of zethrene. The formula (XV) accounts for the properties of zethrene a lot better than the more rigid formula (XIV).

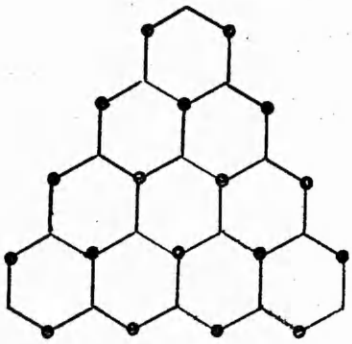
The alternant marking also explains why the isomeric dibenzotetracene cannot exist as a stable hydrocarbon. There are thirteen marked and only eleven unmarked carbon atoms (XVII)



(XIX)



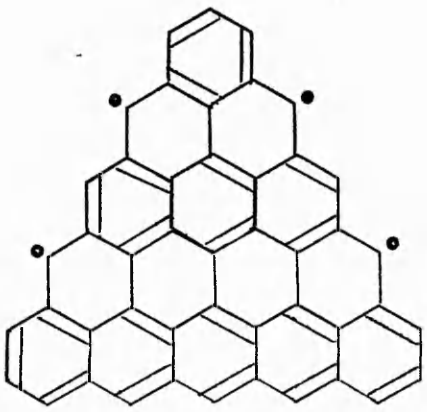
(XX)



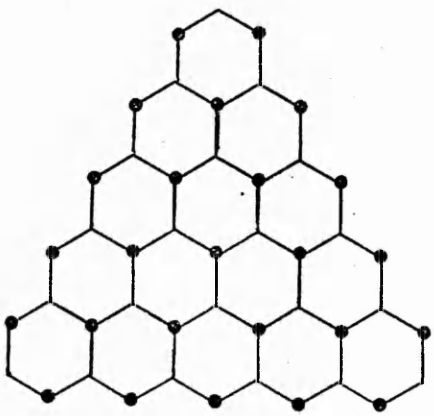
(XXa)

Marked atoms = 18

Unmarked atoms = 15



(XXI)



(XXIa)

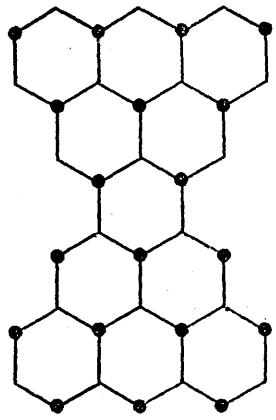
Marked atoms = 25

Unmarked atoms = 21

and it must exist as a diradical in terms of classical chemistry. No hydro-derivative of it has so far been prepared.[14] All the benzologues of zethrene and their corresponding dihydro isomers which have been synthesised, follow the pattern of zethrene and dihydrodibenzotetracene exactly.[8] It should be noted that it is not possible to draw Kekulé structures for molecules such as dibenzotetracene (XVIII), and this method also predicts their existance only as diradicals.

The above idea of alternant marking allows one to predict the stability of a molecule by considering the number of marked and unmarked carbon atoms. As mentioned briefly in the preceding chapter, hydrocarbons which have a triangular shape do not have complete Kekulé structures and exist as radicals. The first member of the series, perinaphthene (XIX) is a fairly stable radical. Triangulene, as discussed, is a diradical which polymerises spontaneously when formed. The next member of the series (XX) with the maximum number of double bonds has three extra valencies, and therefore no Kekulé structure. The alternant marking process (XXa)gives eighteen marked and fifteen unmarked carbon atoms hence both methods predict a threefold radical and the electrons will have parallel spins. Extension to higher homologues predicts fourfold (XXI) and fivefold radicals and so on.

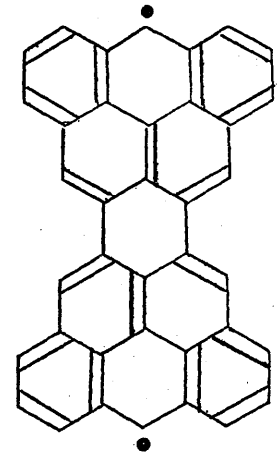
However if one considers the molecule (XXII) which is



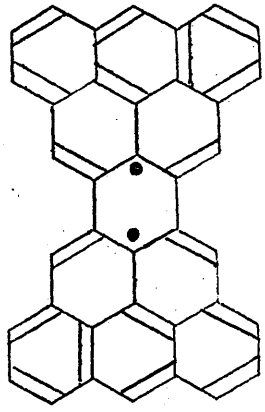
(XXII)

Marked atoms = 19

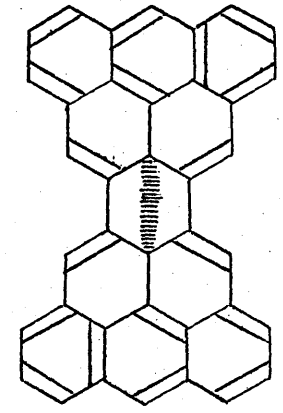
Unmarked atoms = 19



(XXIIa)



(XXIII)



(XXIV)

effectively two triangulene moieties fused together, the number of marked carbon atoms equals the number of unmarked carbon atoms (19 and 19) and on the basis of the alternant marking method this should exist as a stable hydrocarbon. However it is not possible to write even one Kekulé structure for this molecule, and with the maximum number of double bonds it always has two free valencies which cannot be combined to form a conventional bond (XXIIa). Therefore this is a molecule which is predicated to be stable by alternant marking, yet for which no Kekulé structures can be drawn.[15,16]

Longuett-Higgins in his paper dealing with resonance in unsaturated alternant hydrocarbons and in particular triangulene[4], showed using molecular orbital theory that there are three main criteria for the bonding in alternant hydrocarbons. Firstly, there are a least (N-2T) molecular orbitals of zero energy, where N is the number of carbon atoms and T the maximum number of double bonds occuring in resonance structure. This is just the same as the number of carbon atoms which lack double bonds in one or more of the principal resonance structures.

Secondly, that the electrons tend to be confined to those carbon atoms which lack double bonds in one or more of the principal resonance structures.

Thirdly, in the ground state there will be just one electron in each zero energy molecular orbital and if there are two or

more such electrons their spins will be parallel.

The first and last points are very neatly predicted by the simpler alternant method. Obviously if one considers that the π-electrons of the marked atoms all have spins in one orientation, and the unmarked, with spins in the opposite sense, then if the structure has two more marked than unmarked carbon atoms the electrons on these must have spins with the same orientation i.e. parallel spins. Also the number of free valencies for a particular structure will simply arise from this difference in the number of marked and unmarked carbon atoms.

The second point which predicts where the unpaired electrons will most likely be found is not shown by the alternant marking method. However an intuitive consideration of the relative stability of the remaining aromatic part of the molecule, when a particular radical structure is considered, allows one to chose the most likely stable radical. For example perinaphthene with its annulene periphery and the electron in the centre, as shown, seems to be the most likely structure and thus the unpaired electron will be localised for the most part on this carbon atom.

The most interesting feature of structure (XXIIa) is the fact that although there is an even number of marked and unmarked carbon atoms, no matter how one constructs the

maximum number of double bonds (XXIIa) there are always two electrons which cannot be formally bonded, and that these two electrons from alternant marking have opposed spins (XXII). This does not agree with the third criterion which required that the remaining non-bonded electrons would have parallel spins. Thus if a valid comparison of the simple alternant marking method can be made with the more rigorous calculations of Longuett-Higgins there must be a different ground state arrangement.

This also means that in the particular structure (XXIII), the π-electrons on opposite sides of the middle ring have opposed spins. There is the possibility of formation of a Dewar-π-bond across the middle ring involving only these π-electrons, which would not violate the Pauli principle[9] Formation of this bond would allow Kekulé structures to be written for the remainder of the molecule (XXIV) and this should confer stability to the molecule.

In view of this exciting possibility, and in an attempt to clarify the anomolous reaction of the new purple hydrocarbon with maleic anhydride discussed in the last chapter, it was decided to try and synthesise this carbon skeleton unambiguously.

A preliminary molecular orbital calculation has also been carried out by Mr. Howat of this department and indeed does

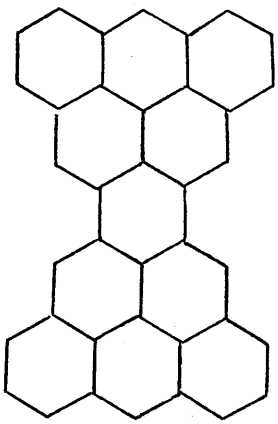
predict that the molecule will exist in a singlet ground state. This is extremely gratifying from both standpoints as it completely vindicates the alternant marking approach which also predicts a singlet state, and adds theoretical support to the above arguement.

Experimental Discussion

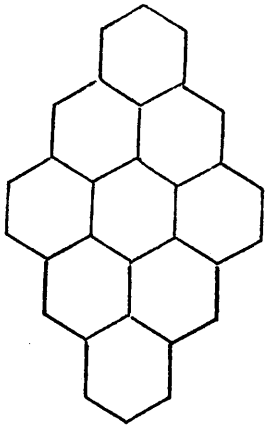
The required structure (XXII)[1] is so closely related to the triangulene skeleton that it seemed reasonable to approach the synthesis in a similar manner to the successful route used by Clar and Stewart in their synthesis of triangulene derivatives.[7,16] In order to try and simplify their approach, the general methods adopted by Scholl and Meyer for the synthesis of 5,6:12,13-dibenzoperopyrene (XXVIII) were also used.[17]

In their initial studies,[16] Clar and Stewart showed that reaction of o-tolylmagnesiumbromide with phthalic anhydride gave only small amounts of the required di-o-tolylphthalide[18] (I), the main product being di-o-tolylbenzene. Reduction of the phthalide (I) with sodium amalgam and alkali gave the required acid (II) which on further oxidation gave the tricarboxylic acid (III) plus a rearrangement product (XIV). Cyclisation of the acid (III) with concentrated sulphuric acid gave the required triketone triangulene skeleton (IV). However small yields from the Grignard reaction and the unfavourable rearrangement during the oxidation discouraged further work in this line.

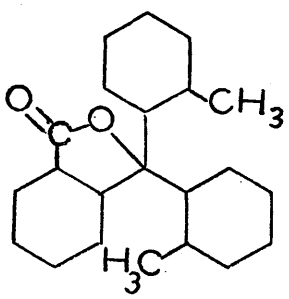
Instead a much better synthetic route starting with tri-o-tolylcarbinol (V) was devised.[7] o-Tolylchloride reacts with o-tolyllithium yielding tri-o-tolylcarbinol, which was partially oxidised to the intermediate phthalide (VI). Further oxidation not only gave the required acid (XIII) but



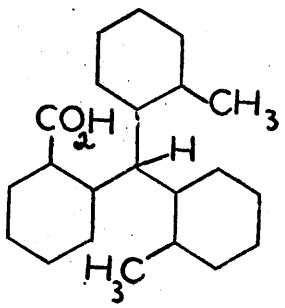
(XXII)



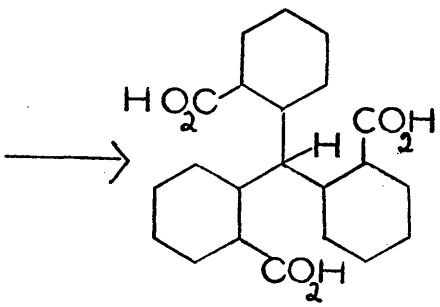
(XXVIII)



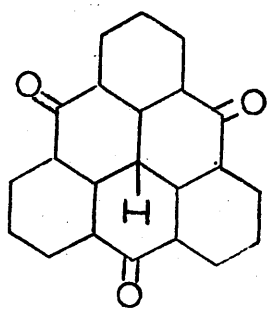
(I)



(II)



(III)

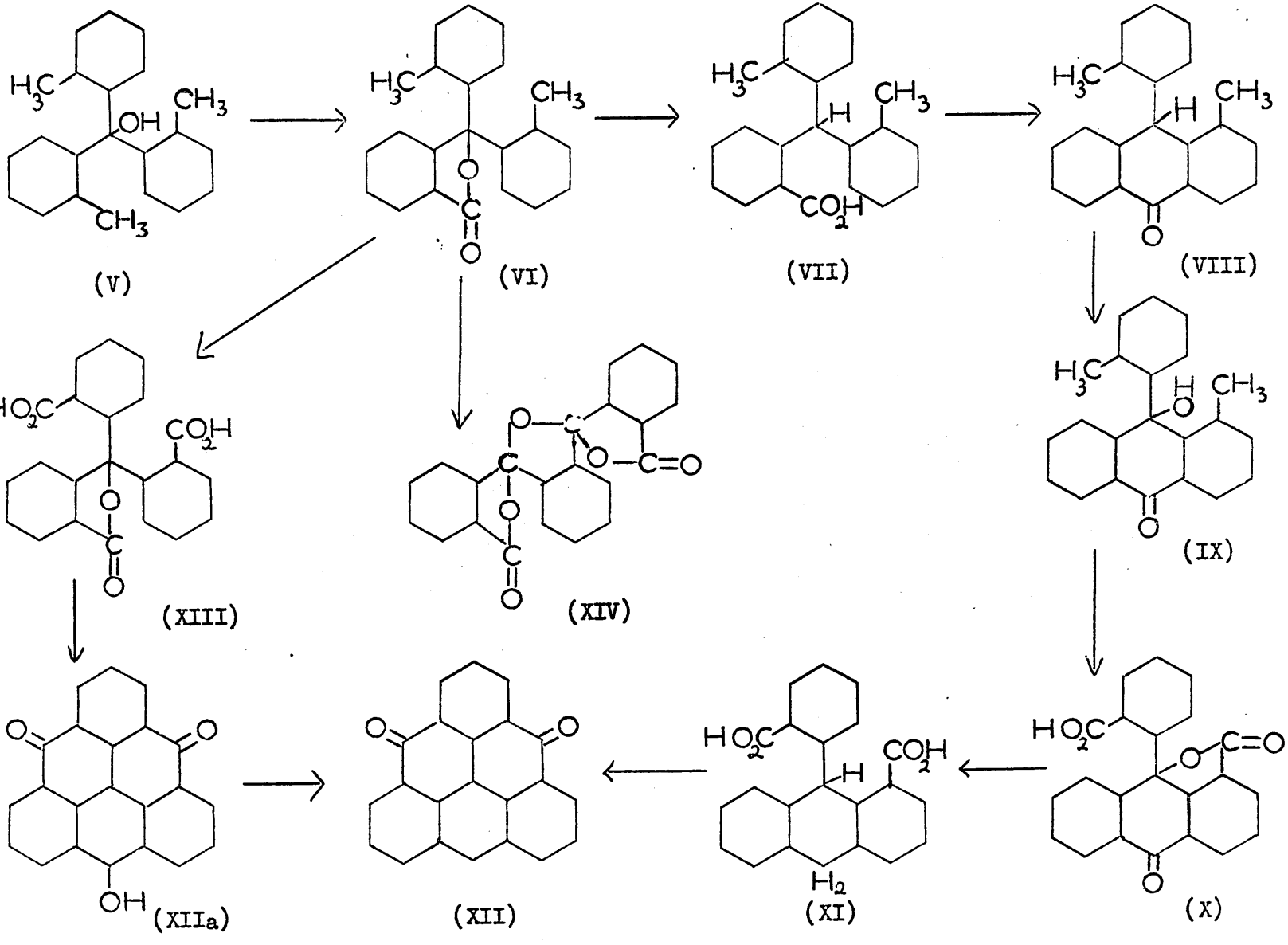


(IV)

also gave a dispiran product (XIV) by rearrangement, which cannot be used in this synthesis, but which proved a very useful intermediate for the synthesis of pure pentaphene.[19] In order to circumvent this problem the stages (VII - XI) were implemented which resulted in the required triangulene-quinone.

In this work an analogous reaction scheme was followed starting with 2,5-dimethylterephthalic acid chloride (XVII). This is readily obtained by oxidising durene (XV) with dilute nitric acid which yields mainly 2,5-dimethylterephthalic acid[20] (XVI). Refluxing the purified acid with thionyl chloride gives the required crystalline acid chloride,[21] which reacts with o-tolyllithium to give the new dicarbinol, di-(dimethyldiphenyl-hydroxymethyl)-p-xylene (XVIII).

In earlier work, attempts were made to reduce tri-o-tolylcarbinol (V) to the known tri-o-tolymethane[22] (XIX) using hydrogen iodide and acetic acid, in the hope that this compound being less sterically hindered might prove easier to cyclise. However an unfavourable cyclisation took place before reduction, resulting in the fluorene derivative (XX), previously isolated by Theilacker and Wessel-Ewald[23] on treatment of the carbinol with hydrochloric acid and sulphuric acid in methanol. Therefore attempts to reduce the dicarbinol (XVIII) to the corresponding hydrocarbon were not pursued.


(V)
(VI)
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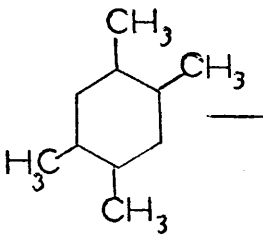
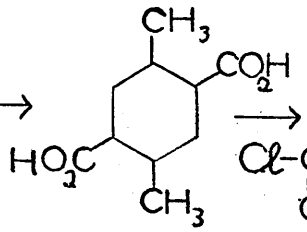
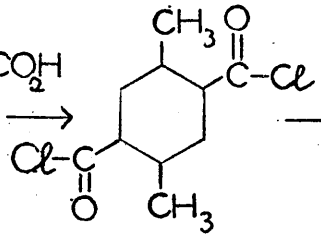


(XV)



(XVI)



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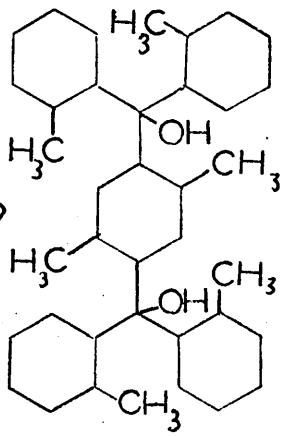

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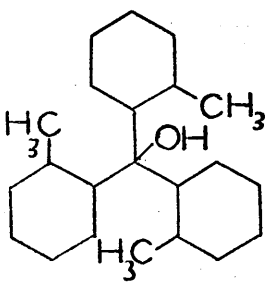

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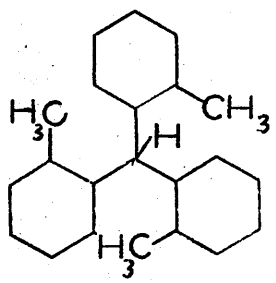
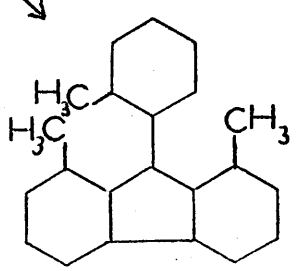


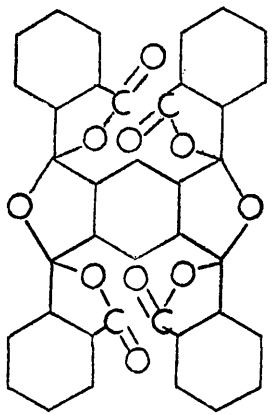
(XIX)



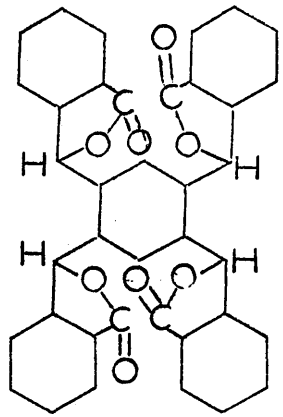
(XX)

The dicarbinol could not be induced to partially cyclise, either by splitting out of two molecules of water when heated to 450° and then subliming the product, or on heating with concentrated sulphuric acid. In both cases the dicarbinol remained unchanged or, at higher temperatures with sulphuric acid, gave sulphonated product.

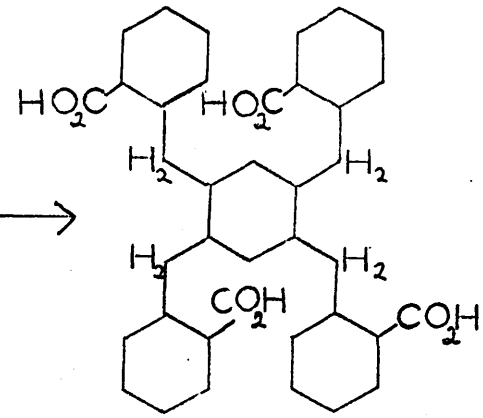
As mentioned the main problem encountered by Clar and Stewart involved the direct oxidation of the intermediates (VI and II). The unusual rearrangement to the dispiran[19] (XIV) resulted in only small yields of the required acid (III, XIII) and necessitated the extra stages (VI to XI). The dicarbinol was therefore oxidised with diluted nitric acid under pressure at 210° , to see if a similar double rearrangement would occur with formation of the double dispiran (XXI). The crystalline product from this reaction gave analysis figures which fitted a molecule with the formula $C_{38}H_{20}O_{12}$. This does not accommodate the double dispiran formula of $C_{38}H_{18}O_{10}$ but fits the normal oxidation product, di-2,5-(diphenyl-o, o'-carboxyhydroxymethyl)-terephthalic acid lactone (XXII). The infra-red spectrum of the carbonyl region shows two carbonyl absorptions at 1780 and 1720cm^{-1} which correspond to an unsaturated γ-lactone and an aryl carboxylic acid group respectively.[24] This infra-red evidence would fit both structures (XXII, XXI) but the evidence from further reduction supports



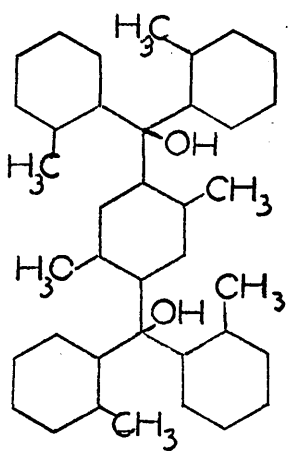
(XXI)



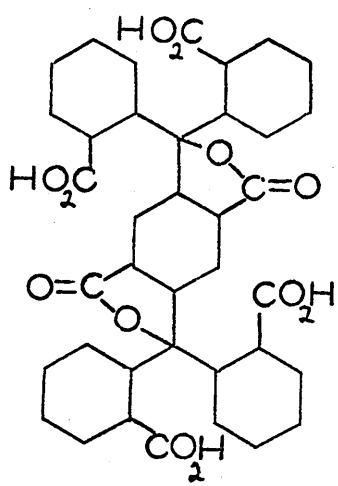
(XXV)



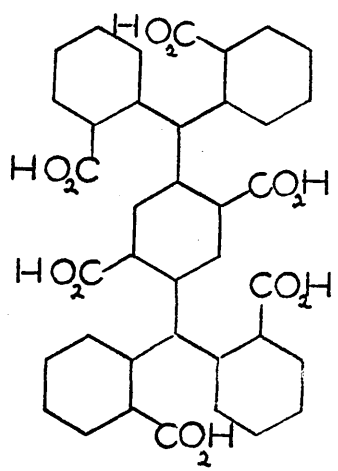
(XXVI)



(XVIII)



(XXII)

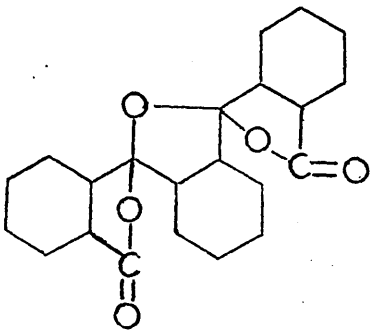


(XXIII)

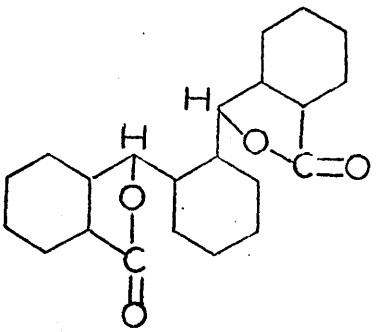
the normal oxidation product (XXII).

The dilactonetetracarboxylic acid was reduced to the hexacarboxylic acid (XXIII) by prolonged treatment with zinc dust and aqueous alcoholic potassium hydroxide. The light brown powder analysed for a molecule with the formula $C_{38}H_{26}O_{12}$ and the infra-red spectrum showed a single broad carbonyl absorption at 1710 cm^{-1} which indicates only free carboxylic acid groups being present in the molecule. This evidence also rules out the double dispiran structure for two reasons. Firstly a similar treatment of the dispiran (XIV) with zinc dust and alcoholic potassium hydroxide yields (XXIV), which still contains two unsaturated γ-lactone moities and would be recognised from the infra-red spectrum. This would also be the case for (XXI) to (XXV). Secondly even if total reduction of the double dispiran were achieved the resulting product (XXVI) would contain too few oxygen atoms to fit the found analysis figures.

In the reaction sequence of Scholl and Meyers work[17] there was no possibility of an oxidative rearrangement and the dilactone (XXVII) was oxidised smoothly in alkaline potassium permanganate to the hexacarboxylic acid (XXIX), which lactonised readily to the structure (XXX). Subsequent reduction with hydriodic acid, red phosphorus and acetic acid yielded the required meso-diphenylanthracene hexacarboxylic acid (XXXI).



(XIV)



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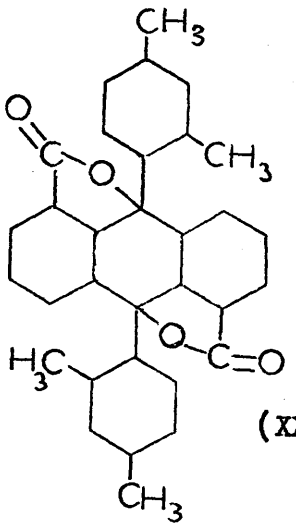

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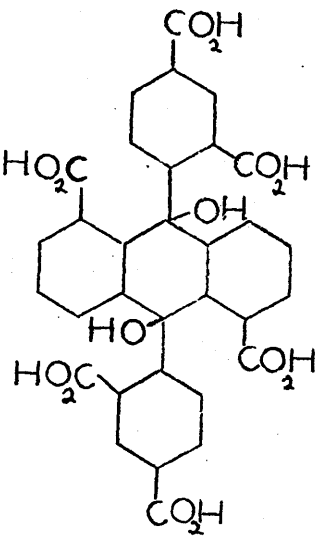
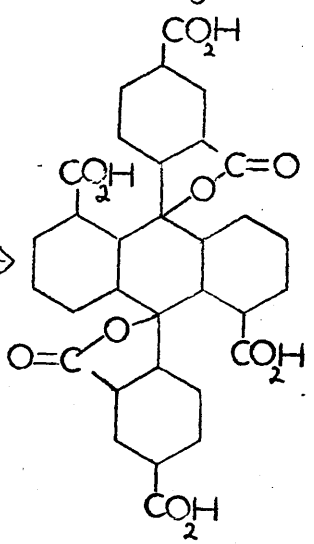
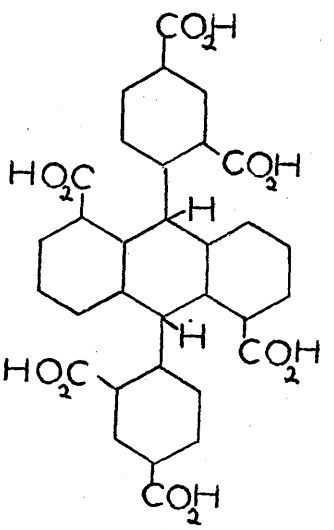


(XXIX)



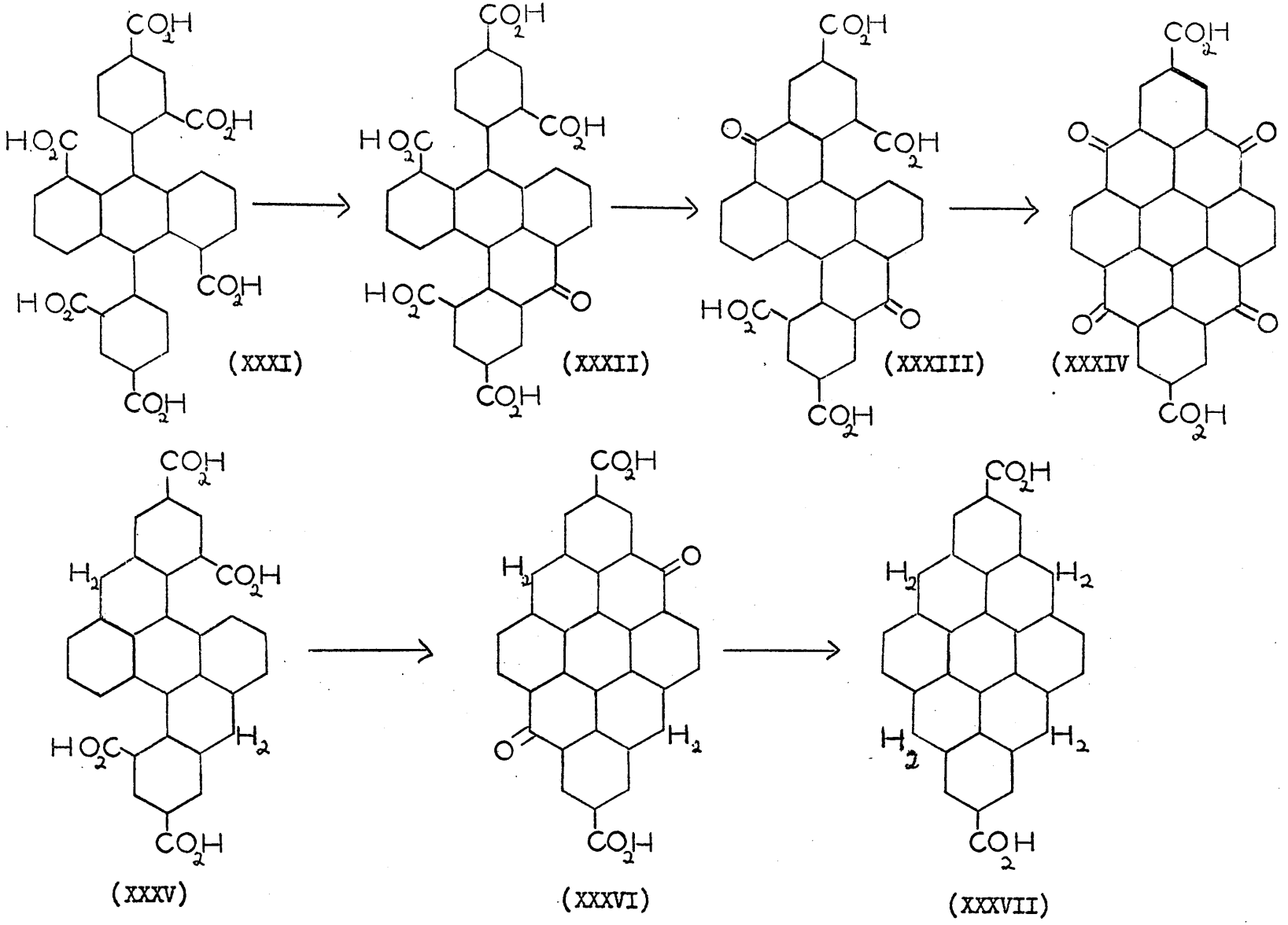
(XXX)



(XXXI)

In our case the overall yield of the hexacarboxylic acid was low, mainly because the dicarbinol could only be oxidised in small amounts in the sealed glass tubes. Therefore attempts were made to improve the yield, by firstly oxidising the dicarbinol under normal reflux with dilute nitric acid and few mls. of nitrobenzene. The alkaline extract was then further oxidised with excess potassium permanganate. However a homogeneous product was not obtained and the pale brown solid product formed a gum even when dried at 100°. After recrystallisation from acetic acid a satisfactory analysis could not be obtained indicating the presence of nitrogen and too much hydrogen. The infra-red spectrum did not show the characteristic symmetric deformation bands of the methyl groups at 1380 cm^{-1} indicating that the methyl groups had been oxidised and the two carbonyl absorptions although much broader than in the product from direct nitric acid oxidation were recognisable. However reduction of this product was not satisfactory and this method of oxidation was abandoned.

In analogy with Scholl and Meyers work and from the triangulene synthesis it was hoped that cyclisation of the hexacarboxylic acid would occur smoothly. However treatment of the acid with concentrated sulphuric acid gave a reddish brown solid at temperatures less than 120°, or a much darker product at higher temperatures which readily dissolved in hot water and was


(XXXI)
(XXXII)
(XXXIII)
(XXXIV)
(XXXV)
(XXXVI)
(XXXVII)

sulphonated product. A satisfactory analysis for the non-sulphonated product was not obtained but was assumed to have partially cyclised from changes in the infra-red fingerprint spectrum. This was disappointing in view of the fact that Scholl and Meyer could even control the extent of cyclisation of their carboxylic acid derivative (XXXI), merely by altering the sulphuric acid concentration, to the structures (XXVII, XXXIII), and could achieve complete cyclisation to the product (XXXIV) by treatment of the intermediate (XXVIII) with pyrophosphoric acid and phosphorus pentoxide at 350°.[17]

In our work this latter process only resulted in charred product when applied to the partly cyclised acid, or when applied directly to the hexacarboxylic acid (XXIII). Under less vigorous conditions however using polyphosphoric acid alone, a product which appeared to be partially cyclised was obtained.

Although their structures were unknown, the products from these two cyclisation attempts were reduced with hydrogen iodide and red phosphorus under pressure.[7] This was hoped to cause reduction and further cyclisation of the molecule in a manner similar to the reaction stages from Scholl and Meyers work as shown (XXXIII - XXXV - XXXVI - XXXVII). In their case, complete cyclisation and reduction to the tetrahydrodicarboxylic acid derivative (XXXVII) was achieved from the partially cyclised intermediate (XXXIII) in one reaction step via the non-isolated

intermediates (XXXV and XXXVI).[17] The extracts from this reaction after chromatography did not crystallise and the U.V. spectrum indicated mainly a benzene derivative with evidence of anthracene and pentaphene derivatives. Both products had similar U.V. spectra but neither could be attributed to a specific isomer.

These products were therefore heated with copper powder at 450°C and sublimed to see if dehydrogenation or further cyclisation would take place. The U.V. spectrum did indicate an increase in the relative amounts of anthracene and pentaphene derivatives but was still a complex mixture. On one occasion, however, the trichlorobenzene extract of the sublimation product did yield a tiny amount of red crystalline product which on redissolving in pure trichlorobenzene gave the spectrum of a substituted anthracene with remarkably sharp intense ρ-bands at 3910, 3710 and 3520Å. The β-bands could not be recorded as the product was virtually insoluble in alcohol, cyclohexane, or even benzene. The sharpness of the ρ-bands and the sparing solubility indicated a condensed hydrocarbon of high molecular weight but this product could not be obtained again and no further physical tests were possible.

Apart from this, all further sublimates were mixtures which could not be satisfactorily separated by chromatography.

Further dehydrogenation of these sublimates was attempted using granulated palladium charcoal.[25] This resulted suprisingly,

in the formation of samples of pure anthracene readily recognised from the U.V. spectrum and mixed melting point with a pure sample.[26] Cyclisation and reduction had taken place but with cleavage of the molecule. All the other products from these dehydrogenations, as experienced throughout these latter stages, were inseparable mixtures which could not be induced to crystallise. T.L.C. plates of these samples in various solvent mixtures indicated more than fifteen spots.

Although there is evidence from the formation of anthracene that partial cyclisation has taken place, there is only very tentative proof from the small amount of red product to indicate anything approaching complete cyclisation to the required structure. This was naturally disappointing especially in view of the comparative ease of cyclisation in the synthesis mentioned. However the intermediate hexacarboxylic acid does require six cyclisations to produce the required skeleton and this may be asking too much, especially when the five carboxyphenyl groups are attached only by single bonds which allow them to adopt out of plane conformations to relieve steric hindrance, but which would reduce the possibilities of cyclisation.

2,5-Dimethylterephthalic acid. (XVI).

This was prepared by dilute nitric acid oxidation of durene following the general method of Schapauff and the crude acid mixture was purified by refluxing with glacial acetic acid which removed the more soluble isomer, 4,6-dimethylisophthalic acid.

The hot acetic acid slurry was filtered, the residue washed with water and dried, giving a white powder which sublimed before melting at 300-340° (Lit. 330-350° sublimes.)[20]

2,5-Dimethylterephthalyl chloride (XVII).

This had been prepared in a pure state previously by de Diesbach on treatment of the pure acid with phosphorus pentachloride. m.pt. 116°.[21] The above acid was refluxed with excess thionyl chloride and a few drops of pyridine for two hours. After distillation of excess thionyl chloride, the solid residue was recrystallised from light petrol (60-80°) twice, giving long colourless prisms. m.pt. (108-112°).

Di-(dimethyldiphenylhydroxymethyl)-p-xylene (XVIII).

Finely cut lithium (8gm.) was added to dry ether (500ml.) under a nitrogen atmosphere, contained in a three-necked flask fitted with a mercury sealed stirrer, reflux condenser and a pressure equalising dropping funnel. A solution of O-bromo-toluene (95gm.) in dry ether (50ml.) was added over 15 minutes

and the resulting mixture stirred for four hours, until most of the lithium had dissolved. The acid chloride(XVII) (17gm.) in ether(100ml.) was added dropwise to the dark brown solution. A vigorous reaction ensued and the solution became dark red. The mixture was allowed to reflux gently for a further hour. The brown-red solution was filtered through a glass wool plug to remove unreacted lithium. The filtered solution was hydrolysed with a mixture of ice and dilute acetic acid and the ether layer washed with water and dried with sodium sulphate (anhydrous). Evaporation of the ether left a light brown gum which on trituration with light petrol (60-80°) furnished a white powder (9gm.). Recrystallisation from light petrol (100-120°) or benzene, yielded colourless prisms m.pt. 249-251° which gave a deep magenta solution with concentrated sulphuric acid.

Found C=86.39%, H=7.38%

$C_{38}H_{38}O_2$ requires C=86.66%, H=7.28%

Attempted dehydration of the diol.

a) The diol (0.2gm.) was heated until it melted and then more strongly under partial vacuum. Bubbling occurred, however no evolution of moisture was observed and a yellow-orange gum sublimed and solidified as a glass. Recrystallisation from light petrol (100-120°) or benzene gave an orange-yellow powder m.pt. 245-248° which dissolved in concentrated

sulphuric acid giving a deep magenta solution.

Found C=86.77%, H=7.37%

$C_{38}H_{38}O_2$ requires C=86.66%, H=7.28%

No change in the U.V. spectrum was observed to account for the orange colour.

b) The diol (0.2gm.) was dissolved in 15ml. of concentrated sulphuric acid and the deep magenta solution warmed for 15 minutes. The solution was cautiously poured into water and the brown precipitate filtered and washed with hot water and dilute ammonia. The solid was extracted with benzene, recrystallised from benzene and light petrol (100-120°) giving a pale brown powder m.pt. 235-245°.

Found C=86.36%, H=7.37%

$C_{38}H_{38}O_2$ requires C=86.66%, H=7.28%

Di-2,5-(diphenyl-9,δ-carboxyhydroxymethyl)-terephthalic acid. lactone (XXII).

The diol (1gm.) and 20% nitric acid (20ml.) were heated together in a sealed tube at 210° for 16 hours. The mixture was diluted with water and the yellow-green amorphous solid filtered, washed thoroughly with water, dried and powdered (0.65gm.) Recrystallisation of the acid proved very difficult, however by

dissolving in the minimum of an acetic acid-water mixture the acid could be precipitated as a white flocculent powder, m.pt. 220-225° (it became honey coloured from 190° until it melted) $\nu_{C=O}$ =1720 cm^{-1} $\nu_{C=O}$ =1780 cm^{-1} The acid dissolved in concentrated sulphuric acid giving a honey coloured solution.

Found C=68.04%, H=3.28%

$C_{38}H_{22}O_{12}$ requires C=67.73%, H=3.14%

Di-2,5-(diphenyl-o,o'-carboxyhydroxymethyl)-terephthalic acid (XXIII).

The above acid-lactone (0.6gm) was dissolved in a solution of 20% ethanolic potassium hydroxide (8ml.) and a few mls. of water were added. Zinc dust (2.5gm.) activated with copper sulphate crystals was added in portions to the refluxing solution and the initial green colour became reddish-brown. After 96 hours the mixture was cooled, diluted with water (10ml.) and filtered twice to remove zinc dust. The brown solution was boiled to remove the alcohol and acidified hot with concentrated hydrochloric acid. The gelatinous precipitate was boiled, filtered, washed with a little water and dried (180mg.). As experienced with the acid-lactone recrystallisation proved difficult, however by dissolving the solid in the minimum of acetic anhydride and adding excess xylene, concentration of this solution furnished a light brown powder m.pt. 195-205°. $\nu_{C=O}$ 1710 cm^{-1} (broad)

The acid dissolved in concentrated sulphuric acid forming a brown solution.

Found		C=67.63%, H=3.94%
$C_{38}H_{26}O_{12}$	requires	C=67.65%, H=3.86%

Attempted cyclisation of the hexacarboxylic acid (XXIII) with sulphuric acid and reduction of the product using red phosphorus and hydrogen iodide (55%).

The acid(0.5gm.) was heated to 150° with concentrated sulphuric acid(15ml.) for a few minutes and the initial brown solution became dark green. The mixture was cooled and a few drops of water were added cautiously forming a reddish purple precipitate. Further water completed the precipitation and the solid was filtered, washed thoroughly with hot water and dried (0.36gm.) The carbonyl region of the I.R. spectrum was much reduced, although there was still an absorption at 1710 $cm.^{-1}$ This product (0.3gm.) was powdered with red phosphorus (0.32gm.), hydrogen iodide (3ml, d=1.7) and potassium iodide (0.15gm.) and heated at 210° for 16 hours in a sealed tube. The contents of the tube were diluted with water and the solid filtered off from the dark brown mother liquor. Preliminary U.V. spectra indicated substituted benzene derivatives, with weak bands at 3500Å and 4700Å. The organic product was dissolved in xylene, filtered dried and the concentrated solution was chromatographed through a short column

of Grade I alumina to remove the dirt. The U.V. spectrum of the five fractions were almost identical with enhancement of the bands at 3570 and 4700Å. Concentration of the solutions failed to yield any crystalline product and the bulked solution was taken to dryness.

Attempted dehydrogenation using copper powder.

The non-crystalline gum from the above reaction (0.2gm.) was mixed with copper powder (0.8gm.) and heated under carbon dioxide at 400° for one hour. The temperature was reduced and a good vacuum was applied to the system. At 290° a yellow gum sublimed followed at 410 (3×10^{-2} m.m.) by a dark reddish-brown product. The temperature was raised to 500° but no further sublimate was observed. The tube was extracted with cyclohexane xylene and trichlorobenzene. The U.V. spectra of the two former extracts were almost identical to the spectra of the starting material. Sharp bands at 3700 and 3910Å which were faintly visible in the xylene spectrum were more intense in the trichlorobenzene extract. The solution contained a very small amount of bright red particles which were filtered, washed with benzene and redissolved in pure trichlorobenzene. The U.V. spectrum showed clearly an anthracene derivative with extremely sharp bands at 3910, 3710 and 3520Å. The low solubility of this product, (β-bands could not be observed in benzene or cyclohexane, although in xylene the β-bands were observed a 3870, 3670 and 3470Å), infers a reasonably high

molecular weight compound but since only this small amount was obtained no further physical measurements could be made. Several repititions of the above procedure failed to produce any more of this product.

Attempted dehydrogenation using palladium charcoal(granular)

The mixture of sublimates obtained after heating (0.5gm.) of partially reduced cyclised hexacarboxylic acid with copper powder as described above, was extracted from the sublimation tube with refluxing xylene. The xylene was distilled off and the remaining gum was sublimed onto several grams of granular palladium charcoal (20%) heated to 350°. After 30 minutes the product was sublimed from the catalyst (3×10^{-2} m.m. Hg.) giving three bands. The initial sublimate, a white crystalline solid was readily soluble in cyclohexane and the U.V. spectrum was identical in every detail to that of pure anthracene. Thus partial cyclisation and dehydrogenation have been accomplished along with cleavage of the molecule. The orange-yellow product, the mixture of the final two sublimates, was also fairly soluble in cyclohexane with bands at 3550 and 3400Å and more intense bands at 3170, 3000 and 2680Å which appeared to be a pentaphene derivative All attempts to afford a separation or to obtain a crystalline product were unsuccessful.

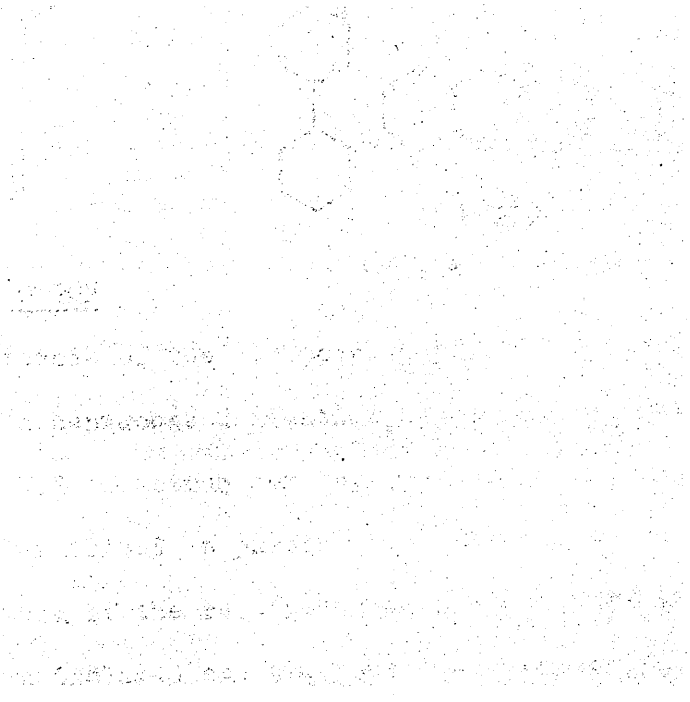
Attempted cyclisation of the hexacarboxylic acid (XXIII) with pyrophosphoric acid and reduction of the product with red phosphorus and hydrogen iodide (55%).

The hexacarboxylic acid (0.5gm.) and pyrophosphoric acid (4 gm.) were powdered together and heated at 250° for 25 mins. under carbon dioxide. The green melt became dark brown. The mixture was poured into water, washed with dil. ammonia and dried (0.41gm.). The product was reduced by heating in a sealed tube at 220° for 12 hours with hydrogen iodide (4ml.), red phosphorus (0.4 gm.) and potassium iodide (0.2 gm.). The resulting solid was powdered and thoroughly extracted with xylene. The solution was passed through a short alumina column to remove the inorganic residues and dirt, and the fractions bulked and taken to dryness. The U.V. spectrum in cyclohexane indicated a pentaphene derivative with bands at 3540, 3380 and 3040Å, and a more intense band at 2860Å which did not belong to the pentaphene spectrum. Nevertheless this appeared to be a more homogeneous solution than from previous reactions.

Dehydrogenation using copper powder and granular palladium charcoal 20%.

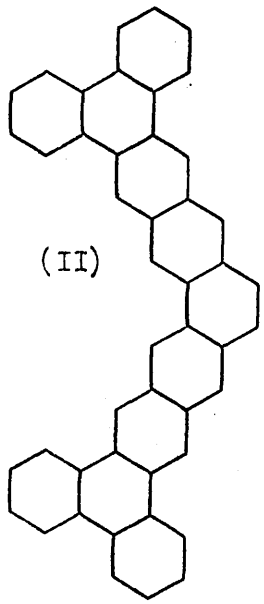
The above product was mixed with copper powder, heated at 400° under carbon dioxide for 2 hours and the resulting mixture sublimed (2×10^{-2} m.m. Hg.). A solution of the reddish brown sublimate in cyclohexane showed a series of bands at 3820(very weak), 3340, 3200, 3060, 2960, 2850 and 2600Å which could not be assigned to any single structure.

Obviously the original pentaphene derivative was now one of a mixture of compounds. The gum was sublimed onto granular palladium charcoal (20%) at 320° and after 30 minutes the product was sublimed from the charcoal (2×10^{-2} m.m. Hg.). Only a very small quantity of yellow orange gum sublimed and the xylene solution showed bands at 3780, 3590, 3420, and 3210Å which indicated an anthracene derivative. The product once again could not be induced to crystallise.

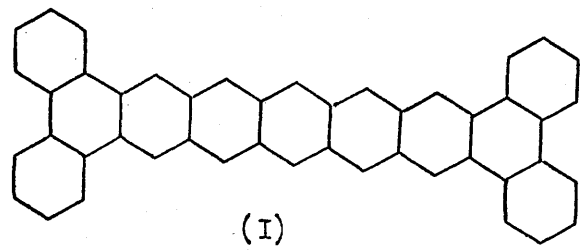


C H A P T E R 5.

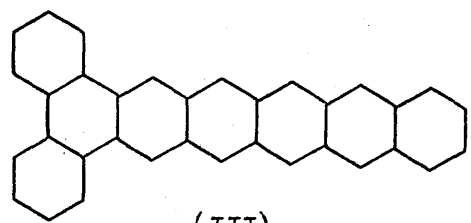
ATTEMPTED SYNTHESIS of 1,2:3,4:11,12:13,14-TETRABENZHEPTACENE .



(II)



(I)



(III)

INTRODUCTION

Synthesis of the hydrocarbon (I) was attempted in order to obtain a heptacene derivative, stable enough, to allow examination of its U.V. spectrum for comparison with the asymmetric annellation effect exhibited in passing from an acene to a tetrabenzacene.

Instead of the required compound a yellow-orange hydrocarbon has been isolated and assigned the structure 1,2:3,4:11,12:13,14-tetrabenzheptaphene (II), on the basis of the similarity of the U.V. spectrum with that of heptaphene. Preliminary attempts to synthesise 1,2,3,4-dibenzhexacene (III) are also described.

Discussion

Before discussing the aim of the work in this chapter in detail a very brief summary of the classification of the bands in the ultraviolet spectra of polycyclic aromatic hydrocarbons will be given.

The bands in the spectra of aromatic hydrocarbons were first divided into three different types - R bands ($\log\varepsilon<2$), B bands (benzenoid bands) and K bands ($\log\varepsilon>4$). Polycyclic aromatic compounds were considered to exhibit only B and K bands.[1] This classification was based on only a limited number of hydrocarbons and never gained acceptance in the field of polycyclic hydrocarbons.

In 1936, Clar[2] introduced a much improved classification which dealt with a larger number of compounds. He pointed out that there were three main band systems which could be divided into α- bands ($\log\varepsilon\sim 2\text{-}3$), p-bands ($\log\varepsilon\simeq 4$) and β-bands ($\log\varepsilon\sim 4\text{-}6$). The characteristic intensities, the shifts on changing phase and polarisation parallel and perpendicular to the molecular axes were all accounted for in this description. However the main feature arising from this method was the formulation of an empirical relationship between the position of the lowest frequency of either the p or β bands which could fit an equation of the form $\sqrt{\frac{R}{\nu}} = n$ where R is a constant and n is an integer (the order number of reciprocal nuclear charges).

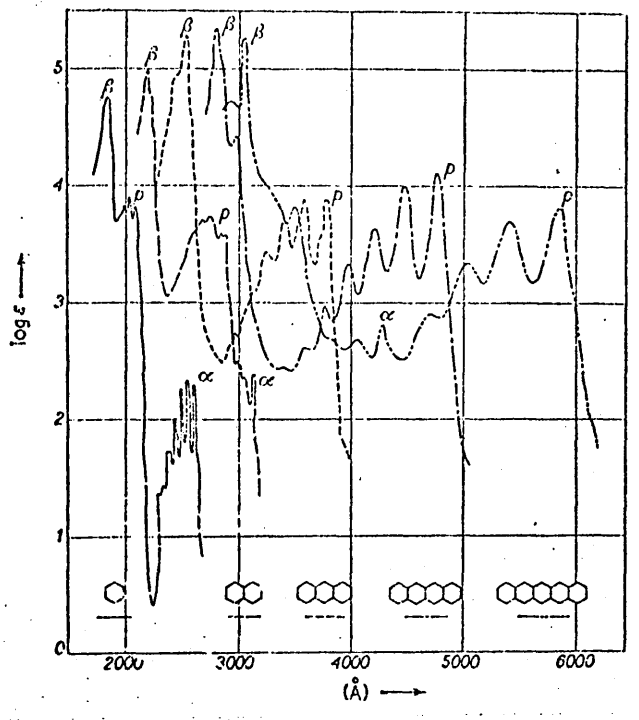

log ε
(Å)
2000
3000
4000
5000
6000
0
1
2
3
4
5
α
β
ρ

Fig. 1.

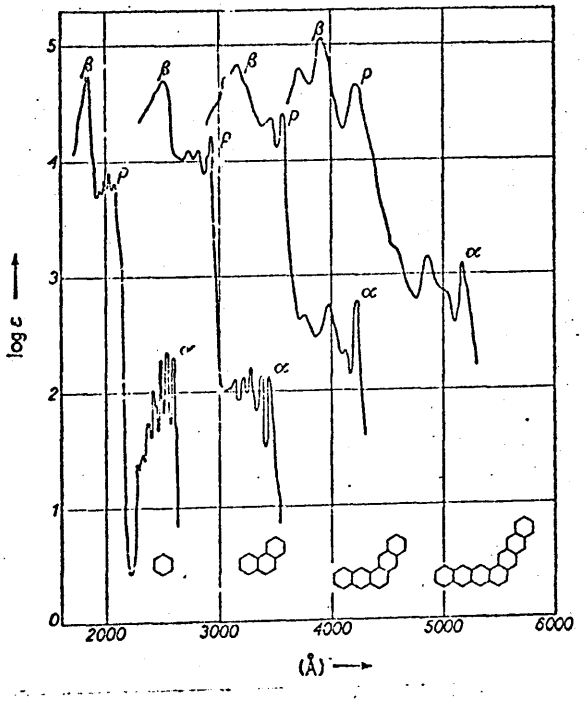

log ε
(Å)
2000
3000
4000
5000
6000
0
1
2
3
5
α
β
ρ

Fig. 2.

From this simple relationship an Annellation Principle has been built up which allows accurate predictions of the bands of unknown polycyclic aromatic hydrocarbons.

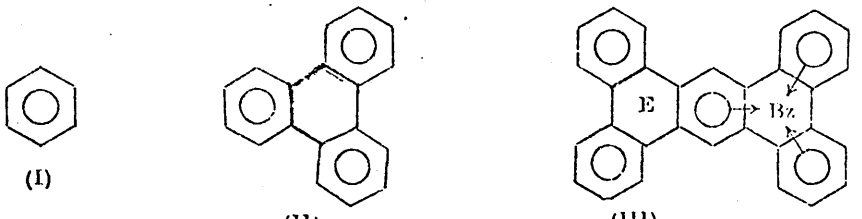
Another classification of these bands has been introduced by Platt,[3] based on a mathematical treatment using the free electron theory of conjugated systems, and this identifies the bands as arising from polarisation in a particular direction with respect to the molecular axes. The two classifications give identical results for the hydrocarbons of the acene series, however with angularly annellated and condensed hydrocarbons the two concepts differ greatly as to the direction of polarisation of certain bands, and to-date the bulk of the evidence[4] rather favours the annellation principle.

Thus Clar and coworkers have synthesised numerous polycyclic aromatic hydrocarbons extending existing series and forming new annellation series which allow a remarkable insight into the electronic conjugation within these molecules.

The simplest series and the most studied is that of the linear acenes, which for the most part show the three characteristic α, ρ and β-bands (Fig. 1). All three bands shift to the red on annellation, although the ρ-bands undergo larger shifts and in anthracene and tetracene overlie and obscure the less intense α-bands. The important relationship in this series applies to both the β and ρ-bands which show an approximately constant

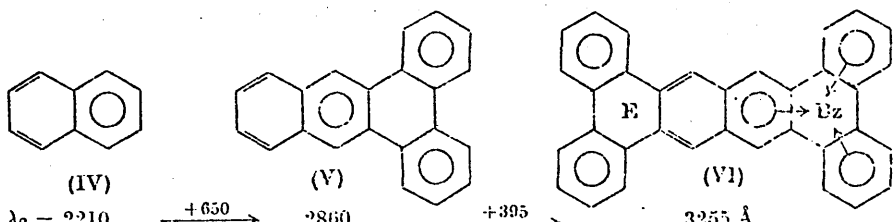
red shift with each successive annellation, conveniently measured in units of $\sqrt{\sigma_A}$, the scale for reciprocal nuclear charges (i.e. the π-electrons which come into the system to counteract nuclear attraction).[5] This regular bathochromic shift is therefore classified as a symmetric annellation effect. A similar straight forward relationship exists for the α and β-bands of the angularly arranged phene series (Fig. 2), although again the α-bands are sometimes hidden. Consideration of the spectra of the phenes shows that the shift difference in Å experienced by the β-bands is also approximately constant.[5] However dealing with molecules which have several angularly annellated rings the situation is more complex and results in irregular effects which are termed asymmetric annellations. In this particular work it was hoped to obtain further evidence for the asymmetric effect shown in building up symmetrical tetrabenzacenes from the corresponding acenes.[6]

The successive condensation of two diphenyl complexes to an acene produces two significantly different bathochromic shifts.[7] Addition of the first diphenyl complex to benzene (I) forming triphenylene (II) results in a shift of the β-band of 718Å or $7.60\sqrt{\text{Å}}$. The second addition forming tetrabenzanthracene (III) is marked by a much smaller shift of 355Å or $3.40\sqrt{\text{Å}}$. This asymmetry can readily be explained by the sextet theory, where a quantitative assessment of the degree of aromatic conjugation in an induced sextet, as indicated by the arrows, can be made



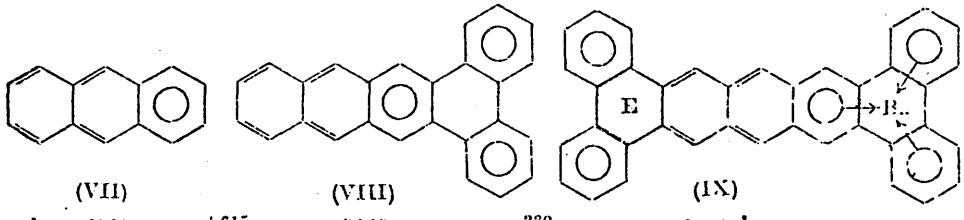
(I) (II) (III)

$\lambda_\beta = 1852$	$\xrightarrow{+718}$	2570	$\xrightarrow{+355}$	2925 Å
$\sqrt{\lambda_\beta} = 43{\cdot}04$	$\xrightarrow{+7{\cdot}66}$	50·70	$\xrightarrow{+3{\cdot}40}$	$54{\cdot}10\sqrt{}$Å
		$50{\cdot}70 - 3{\cdot}40 = 47{\cdot}30\,\widehat{=}$		2237 Å
		β-Band of naphthalene, found		2210 Å



(IV) (V) (VI)

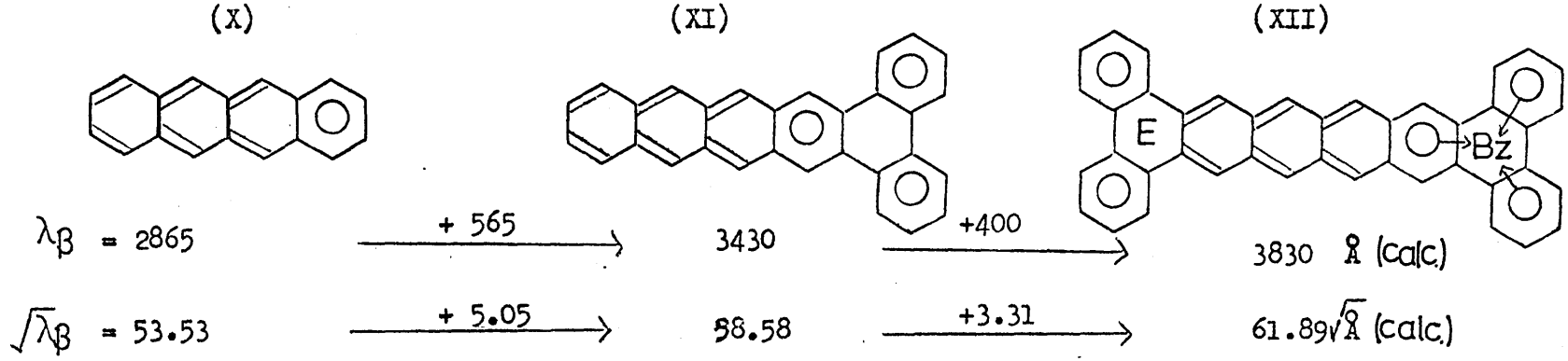
$\lambda_\beta = 2210$	$\xrightarrow{+650}$	2860	$\xrightarrow{+395}$	3255 Å
$\sqrt{\lambda_\beta} = 47{\cdot}01$	$\xrightarrow{+6{\cdot}47}$	53·48	$\xrightarrow{+3{\cdot}57}$	$57{\cdot}05\sqrt{}$Å
		$53{\cdot}48 - 3{\cdot}57 = 49{\cdot}91\sqrt{}$Å $\widehat{=}$		2491 Å
		β-Band of anthracene, found		2515 Å

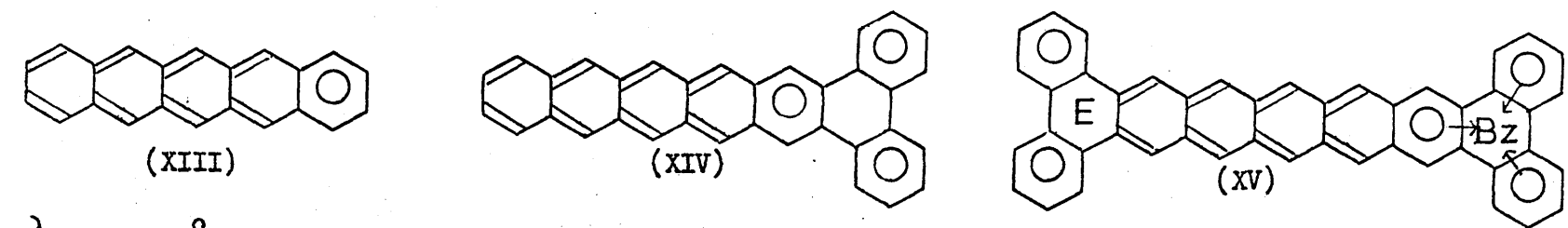


(VII) (VIII) (IX)

$\lambda_\beta = 2515$	$\xrightarrow{+615}$	3130	$\xrightarrow{330}$	3460 Å
$\sqrt{\lambda_\beta} = 50{\cdot}15$	$\xrightarrow{+5{\cdot}80}$	55·95	$\xrightarrow{2{\cdot}87}$	$58{\cdot}82\sqrt{}$Å
		$55{\cdot}95 - 2{\cdot}87 = 53{\cdot}08\sqrt{}$Å $\widehat{=}$		2818 Å
		β-Band of tetracene, found		$\frac{2930}{2740}$ } 2865 Å

Fig. 1.





$\lambda\beta$ = 3030 Å

$\sqrt{\lambda\beta}$ = 35.05$\sqrt{Å}$

Fig. 1. (cont.)

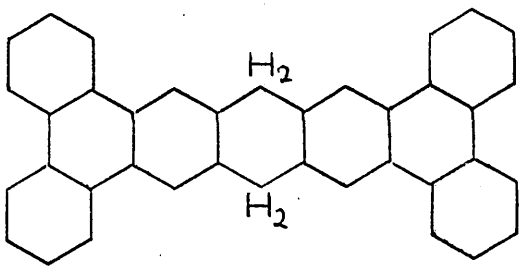
by a simple subtraction rule. If the second shift going from triphenylene to tetrabenzanthracene is subtracted from the β-band of triphenylene, then effectively the influence of the two external benzo rings is removed leaving only pure aromatic conjugation. This $50.70-3.40 = 47.30\sqrt{\text{Å}}$. This wavelength is practically identical with the observed β-band of naphthalene at 2210Å. The benzene system has thus not been extended to the π - electron system of anthracene but only to the naphthalene system. In terms of π-electron conjugation, the induced sextet is equivalent to one ring in the acene series, while an empty ring marked 'E' is produced during the second annellation.[6,7]

This is further exemplified in the series naphthalene (IV) to tetrabenztetracene (VI). The first diphenyl complex leading to 1,2:3,4-dibenzanthracene (V) causes a large shift of 650Å or $6.47\sqrt{\text{Å}}$, while the second condensation resulting in the formation of 1,2:3,4:7,8:9,10-tetrabenzotetracene (VI) produces a smaller shift of 395Å. Application of the subtraction rule gives $53.48-3.57=49.91\sqrt{\text{Å}}$ or 2491Å which is almost equal to the observed β-band of anthracene at 2515Å. Again the π-electron system of naphthalene has only been extended to the anthracene system and an empty ring E produced by the second addition leading to tetrabenzotetracene. This trend is repeated in the series from anthracene (VII) to 1,2:3,4:8,9:10,11-tetrabenzo-pentacene (IX) where the subtraction rule $55.59-2.8=53.08\sqrt{\text{Å}}$

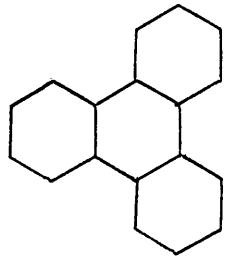
or 2818Å gives a predicted β-band in excellent agreement with the split β-band of tetracene (2740 and 2930Å).[6,7] The next series from tetracene (X) to tetrabenzhexacene (XII) is not complete as tetrabenzhexacene has not been synthesised. However following the subtraction rule, one can calculate where the β-band of this hydrocarbon will be from comparison of tetracene (X) and dibenzopentacene (XI) as shown. Fig1.

It was therefore of interest to attempt the synthesis of the hydrocarbons 1,2:3,4-dibenzohexacene (XIV) and 1,2:3,4:10,11:12,13-tetrabenzheptacene (XV) which are the remaining members of the last series shown starting with pentacene (XIII).
These two hydrocarbons are also of considerable interest in their own right as they are possible stable derivatives of the extremely reactive parent hydrocarbons, heptacene and hexacene. Although hexacene has been prepared in a pure state it is so reactive that a complete spectrum has not been obtained, and all attempts to synthesise heptacene have been unsuccessful.[8]

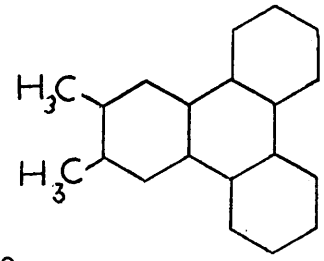
A sparingly soluble yellow-orange hydrocarbon has been obtained which was initially thought to be 7,16-dihydrotetrabenzheptacene (XVI) on the basis of the U.V. spectrum, analysis and mass spectrum. The mass spectrum showed a small peak at 580 with a larger peak at 578 which were attributed to the dihydroderivative and the parent ion minus two hydrogen atoms respectively. The initial analysis also fitted the formula $C_{46}H_{28}$ rather than the fully



(XVIII)



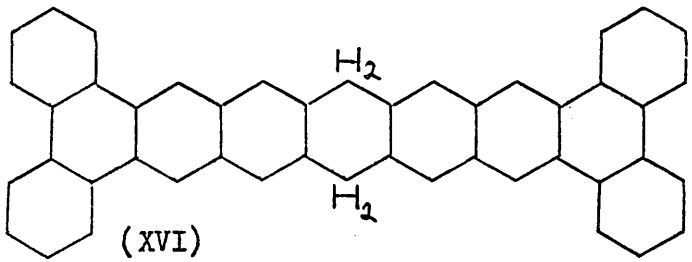
(XIX)



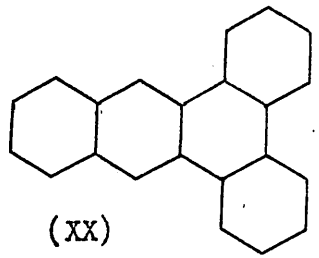
(XVII)

$\lambda\alpha$ = 3470 ← +70 — 3840 — +40 → 3440 Å

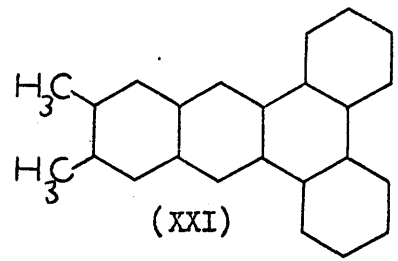
$\lambda\beta$ = 2910 ← +70 — 2840 — +20 → 2860 Å



(XVI)



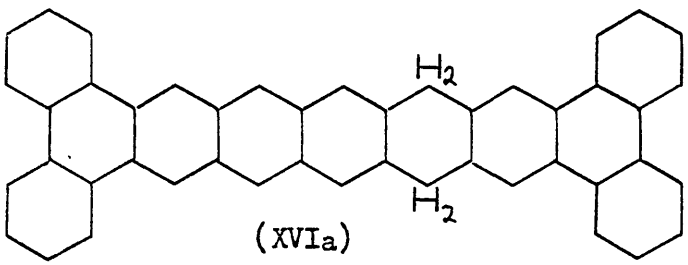
(XX)



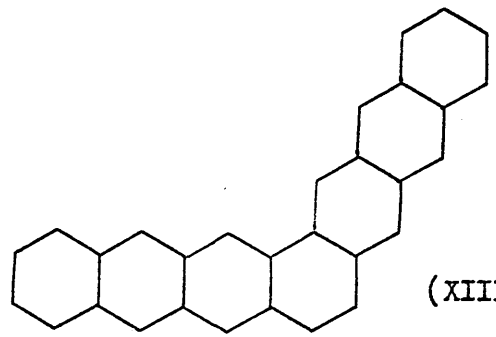
(XXI)

$\lambda\alpha$ = 4060 ? ← +320 — 3740 — +40 → 3780 Å

$\lambda\beta$ = 3810 ? ← +320 — 3490 — + 0 → 3490 Å



(XVIa)



(XIII)

aromatic $C_{46}H_{26}$. However all attempts to dehydrogenate this compound were unsuccessful.

There was however an anomaly in the U.V. spectrum. Comparison of dihydrotetrabenzopentacene[9] (XVIII) and 2,3-dimethyltriphenylene (XVII) with the parent triphenylene (XIX) showed the usual small bathochromic shifts of 20-40Å associated with the introduction of alkyl substituents. A similar comparison of 6,7-dimethyl-dibenzanthracene (XXI) and the above derivative (XVI) with the parent hydrocarbon dibenzanthracene (XX), required a shift of the α-band by 320Å for dihydrotetrabenzheptacene (XVI), while only the usual small shift was observed in the case of 6,7-dimethyl-dibenzanthracene (XXI). Furthermore the log ε value of the band at 4060Å which was considered to be an α-band was found to be 4.81 which is too high for an α-band but fits for a ρ-band.[2] Re-examination of the spectrum of a more concentrated solution revealed the α-bands at 4780,4640 and 4480 which had originally been attributed to a small amount of the isomeric dihydro-tetrabenzheptacene (XVIa). The complete spectrum is shown in Fig. 1 and bears a remarkable similarity to the spectrum of the known heptaphene[10] (XXII) Fig. 1.

Unfortunately, however, there are no examples of phene structures which have this tetrabenzo annellation at the terminal rings. Therefore a direct comparison with an annellation series or with an analogous compound is not possible. Nor is it justifiable to

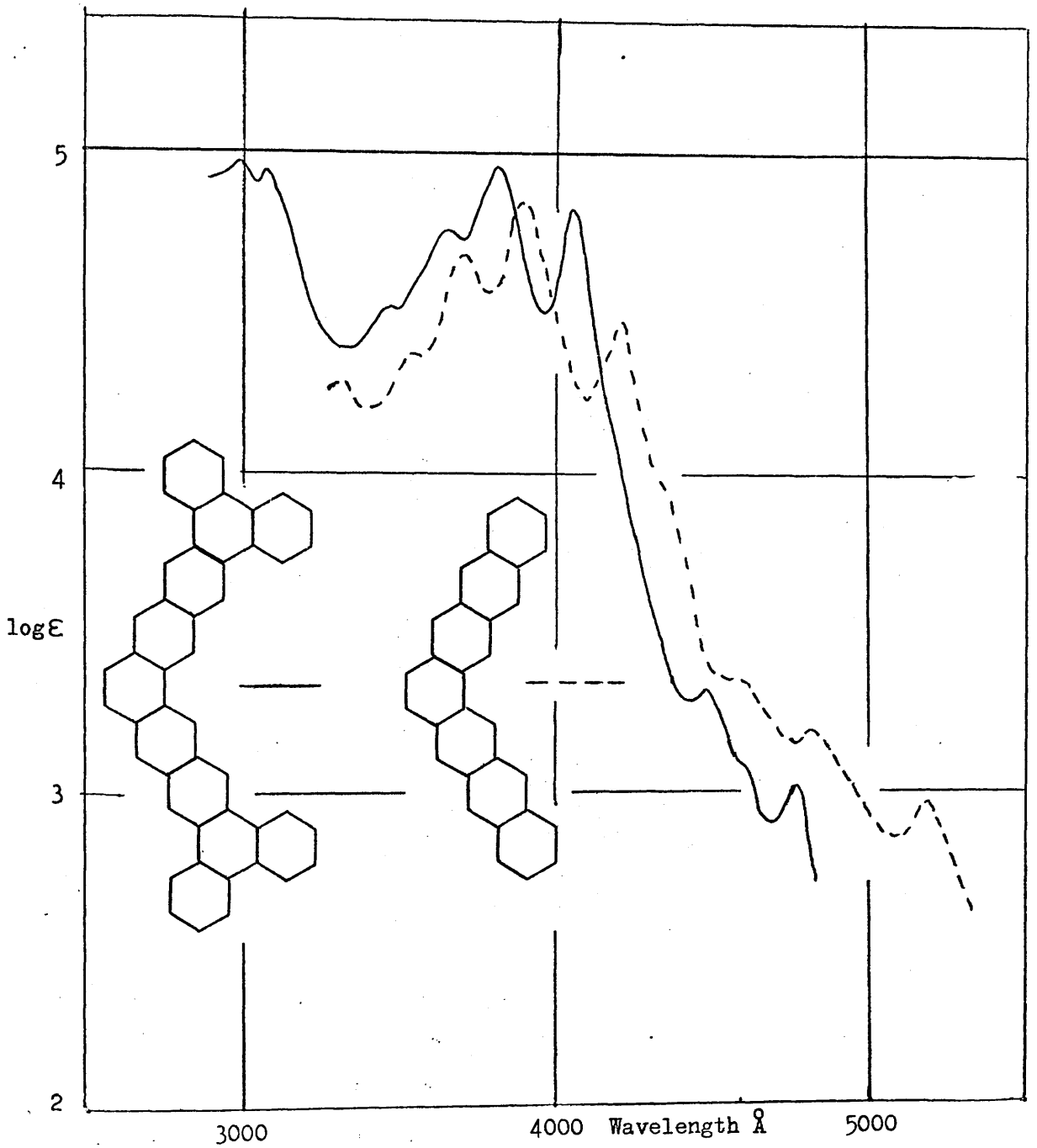
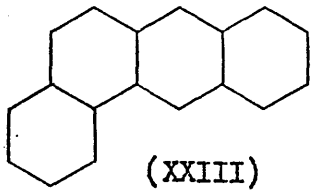
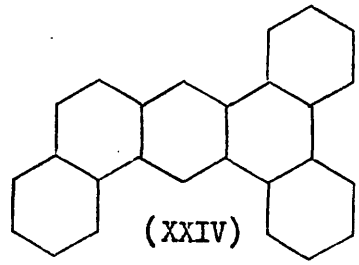


Fig.1 Absorption max. (Å) and log ε (in parentheses).
——— 1,2:3,4:11,12:13,14-Tetrabenzheptaphene in xylene.
α :4780(3.02),4640(3.03),4480(3.31); ρ :4060(4.81); β :3810(4.95)
3660(4.70),3480(4.52); β′ :3080(4.93),2990(4.97)
- - - - Heptaphene in trichlorobenzene α :5190(2.94), 4870(3.16),
4570(3.34); ρ :4220(4.47); β :3900(4.83), 3700(4.67).



(XXIII)

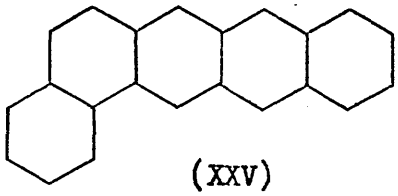


(XXIV)

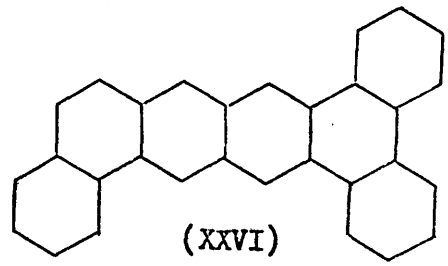
$\lambda\alpha$ = 3850 —(+ 30)→ 3880 Å

$\lambda\rho$ = 3590 —(− 140)→ 3450 Å

$\lambda\beta$ = 2900 —(+ 140)→ 3040 Å



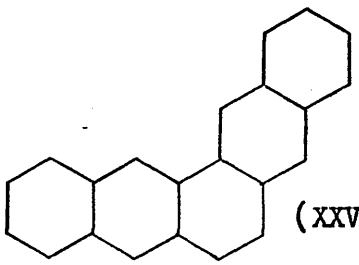
(XXV)



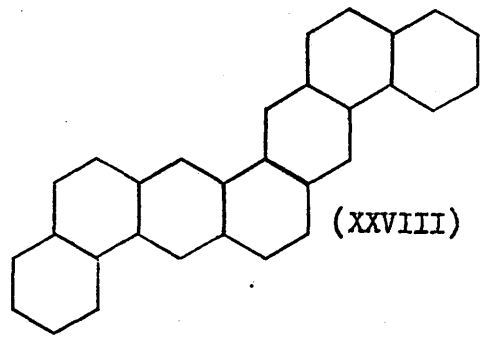
(XXVI)

$\lambda\rho$ = 4250 —(− 20)→ 4230 Å

$\lambda\beta$ = 3190 —(+ 90)→ 3280 Å



(XXVII)



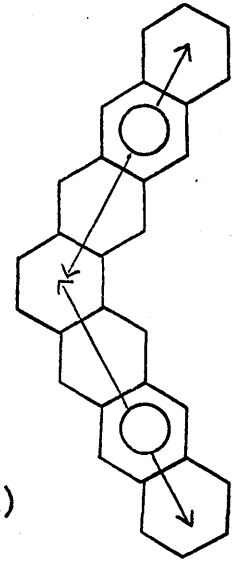
(XXVIII)

$\lambda\alpha$ = 4250 —(− 20)→ 4230 Å

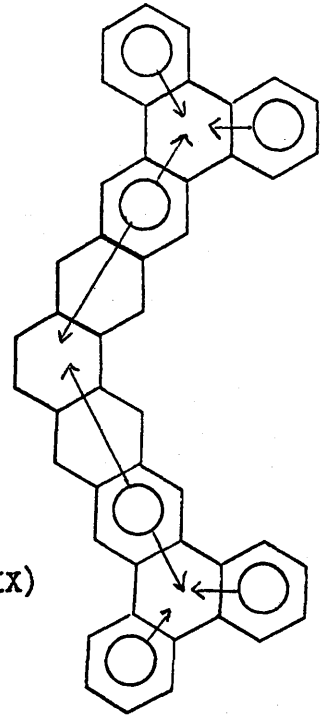
$\lambda\rho$ = 3580 —(+ 100)→ 3680 Å

$\lambda\beta$ = 3160 —(+ 100)→ 3260 Å

(XIII)



(XXIX)



$\lambda_\alpha = 5180$ —400→ 4780 Å

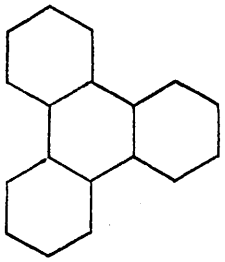
$\lambda_\rho = 4200$ —140→ 4060 Å

$\lambda_\beta = 3880$ —70→ 3810 Å

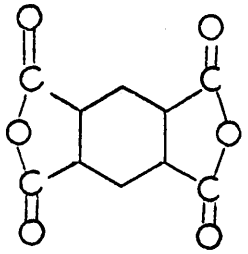
compare it with the shifts observed in the tetrabenzacene series already discussed.

In comparison with heptaphene, all three bands have shifted to the violet; the α-band considerably by 400Å, the ρ-bands by 140Å and a smaller hypsochromic shift of 70Å for the β-band. Although information regarding shifts of α-band is sparse due to the fact that they are so often obscured by ρ-bands, the shift of the α-band in this case is very large in comparison with that of the β-band. Further the violet shift of the β-band does not conform with the vast amount of information accumulated for the behaviour of the β-band on annellation. In all cases annellation of two or four rings to the terminal ring or rings results in a red shift for the β-bands. This is shown in the examples (XXIII)(XXIV),(XXV)(XXVI),(XXVII)(XXVIII) and although the shift is on occasions small, it is consistently to the red. However the shift of the β-band to the violet in this case is very small, 70Å and the overall similarity of the spectrum to that of heptaphene has led to the tentative assignment of the structure as 1,2:3,4:11,12:13,14-tetrabenzheptaphene (XXIX).

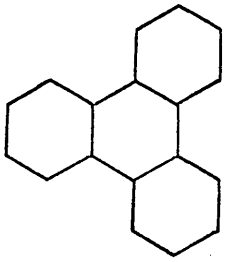
Finally, preliminary work on a new synthetic scheme for adding four rings linearly to a molecule, in particular with a view to synthesising dibenzhexacene is described in the following discussion.



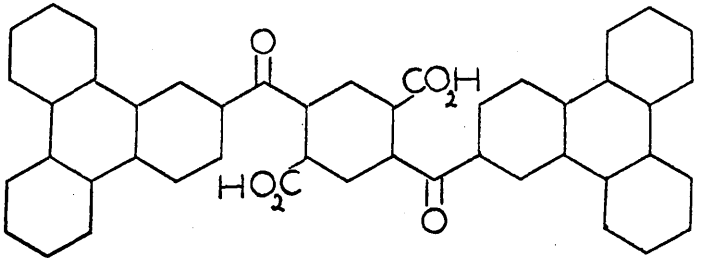
(XIX)



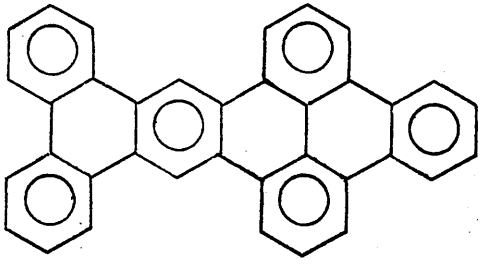
(XXX)



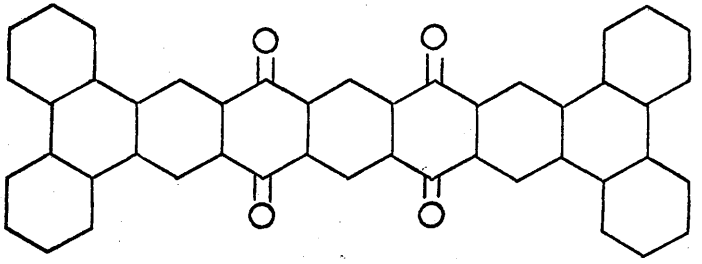
(XIX)



(XXXI)



(XXXIII)

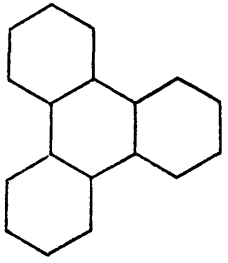


(XXXII)

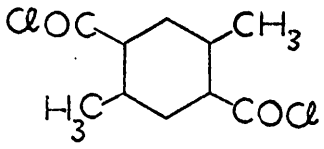
Experimental Discussion

When considering a synthetic scheme for a highly symmetrical polycyclic aromatic hydrocarbon such as tetrabenzheptacene one of the best methods involves condensation of two suitably substituted derivatives which are each half of the required compound. A similar method especially when the linear part consists of an odd number of rings, involves double condensation of two identical molecules to a single central ring.[11]

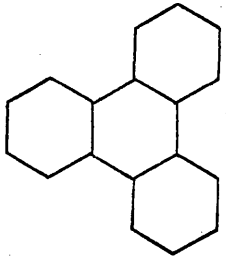
The latter method was adopted in this case and the initial work involved a Friedel-Crafts condensation of two molecules of triphenylene (XIX) with a molecule of pyromellitic dianhydride (XXX) using aluminum trichloride. However, with benzene and o-dichlorobenzene as solvents the yields of the doubly condensed isomer (XXXI) were very small, a mono derivative and unreacted triphenylene being the major constituents even after prolonged reaction time. The latter solvent has been found particularly useful for less soluble compounds,[12] but did not improve the yield of the required isomer in this case. In tetrachloroethane at higher temperatures (75-85°) the main product was a pale yellow extremely insoluble compound, which proved on U.V. examination to be the known 1,2:3,4:6,7:12,13-tetrabenzopentacene[13] (XXXIII). In this reaction the triphenylene has not reacted with the anhydride but has undergone self-condensation.



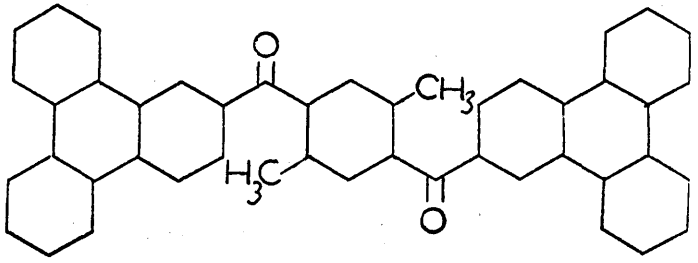
(XIX)



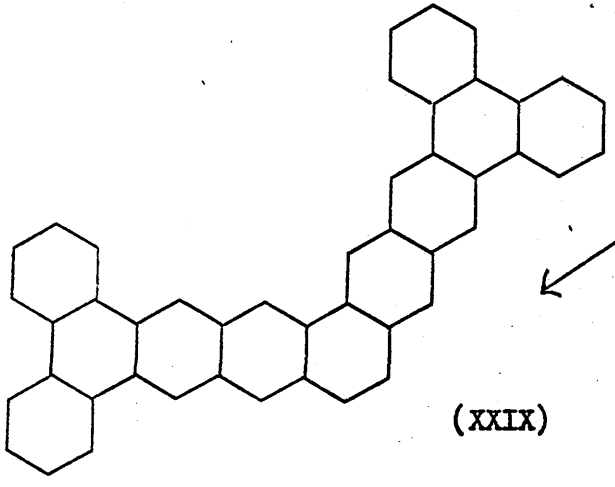
(XXXIV)



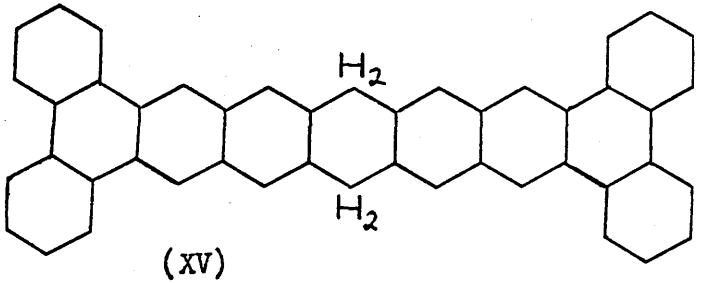
(XIX)



(XXXV)



(XXIX)



(XV)

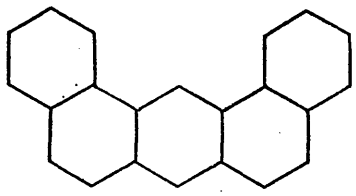
Despite the poor yields, attempts were made to cyclise the crude reaction mixtures from the Friedel-Crafts reaction in the hope of isolating the required diquinone which would be rather insoluble. Boiling the crude acid mixture with benzoyl chloride and a trace of sulphuric acid,[14] gave a colour change from green, through a short lived intermediate blue, to a final wine colour, but gave no evidence of the required diquinone (XXXII). A harsher cyclisation, by adding fresh phosphorus pentoxide to a refluxing solution of the crude acid and phthalic anhydride was also carried out.[16] Sublimation of the crude reaction product gave a mixture of compounds none of which gave an analysis corresponding to the diquinone. A small quantity of extremely insoluble pale yellow needles which only sublimed at very high temperatures, although not characterised, were assumed to be the required compound.

Direct reduction of the crude cyclised product was also attempted using zinc dust and alcoholic sodium hydroxide solution.[15] Sublimation of the product yielded only a small amount of product and this did not give a satisfactory hydrocarbon analysis. The bulk of the product remained unsublimed even at 500°. The poor yield of the required intermediate (XXXI) could not be improved by increasing the reaction temperature or by changing the solvent and this reaction scheme was discontinued.

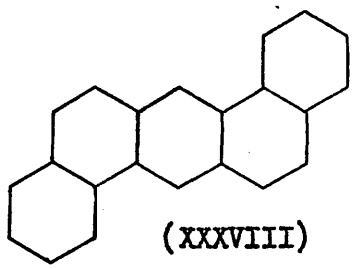
In order to improve the yields of the initial stage, the

Friedel-Crafts condensation of 2,5- dimethylterephthalyl chloride (XXXIV) with two molecules of triphenylene (XIX) yielded the intermediate ketone (XXXV). As the acid chloride had been purified previously this should lead to only one ketone and it was expected that condensation involving an acid chloride would be more efficient than the above anhydride. This reaction scheme had been used successfully in the synthesis of dihydro-1,2- benzhexacene.[17]

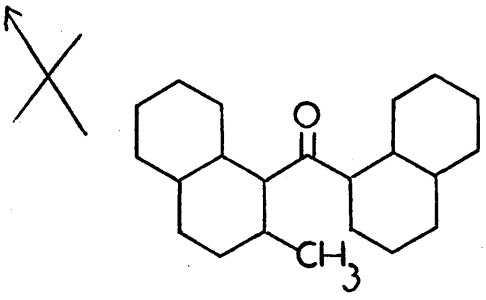
The ketone isolated from the condensation had a sharp melting point and appeared to be a uniform compound. Pyrolysis of the ketone[18] alone, in a sublimation tube under carbon dioxide gave firstly small amounts of unreacted starting material, triphenylene and small amounts of a tetracene derivative. The residue was sublimed using a high vacuum and yielded a pale orange sublimate which was partially purified by refluxing with xylene, which removed more soluble impurities. As mentioned earlier, the initial U.V. spectra, mass spectrum and the analysis which fitted a molecular formula of $C_{46}H_{28}$ favoured the dihydrotetrabenzheptacene structure (XV). However, not suprisingly in the light of the new U.V. evidence, all attempts to dehydrogenate the molecule were unsuccessful, resulting in unchanged hydrocarbon or decomposition at higher temperatures. Also an attempt to add maleic anhydride to the molecule by refluxing with xylene left the hydrocarbon unreacted. This can be compared with



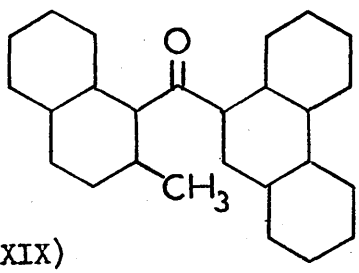
(XXXVII)



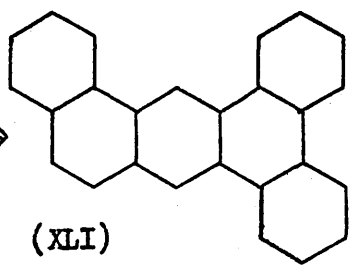
(XXXVIII)



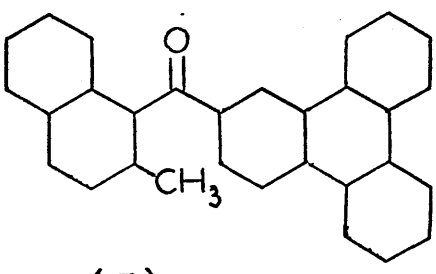
(XXXVI)



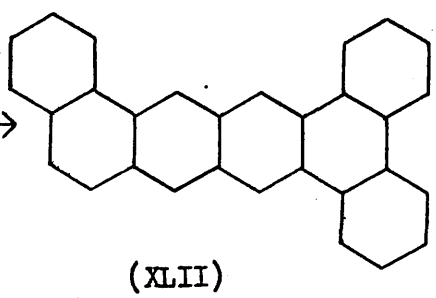
(XXXIX)



(XLI)



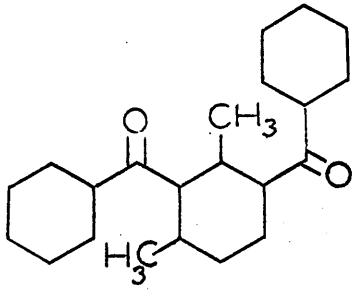
(XL)



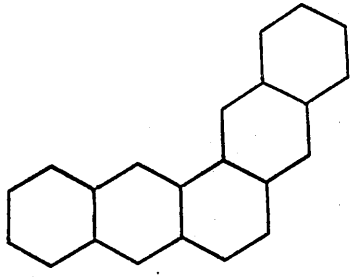
(XLII)

heptaphene which does add two molecules of maleic anhydride under these conditions.[10] However the four annellated rings in tetrabenzheptaphene (XXIX) have introduced four new inherent sextets, and the molecule is more benzenoid in character than heptaphene and therefore more reluctant to add maleic anhydride. Addition only takes place when the hydrocarbon is refluxed with maleic anhydride alone.

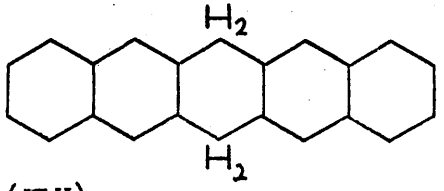
Thus despite the fact that the original acid chloride was considered to be the single isomer (XXXIV), the unexpected angular tetrabenzheptaphene appears to have been formed. If the ketone was infact the single isomer then rearrangement must have occured during pyrolysis. Although this is common in such cases as (XXVI) (XXXVII), (XXXVIII) it is generally considered that migration is only favoured if a trans-bisangular hydrocarbon can be formed in place of the cis-bisangular isomer.[19] Thus pyrolysis of ketones (XXXIX) and(XL) to give 1,2:3,4:5,6-tribenzanthracene (XLI) and 1,2:3,4:7,8-tribenzotetracene (XLII) takes place without rearrangement, and there is therefore no apparent reason for the ketone rearranging in this case. However, the formation of pentaphene (XLIV) by pyrolysis of the ketone (XLIII), also results in small amounts of dihydropentacene (XLV) which could only be formed by rearrangement.[20] Therefore an analogous rearrangement must have occured in our case to explain the observed product (XXIX) from the pure intermediate ketone(XXXV).



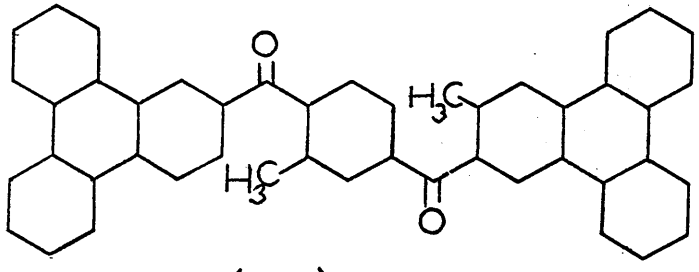
(XLIII)



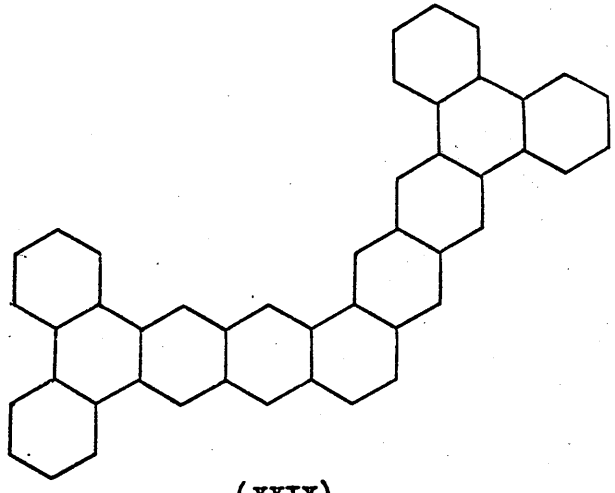
(XLIV)



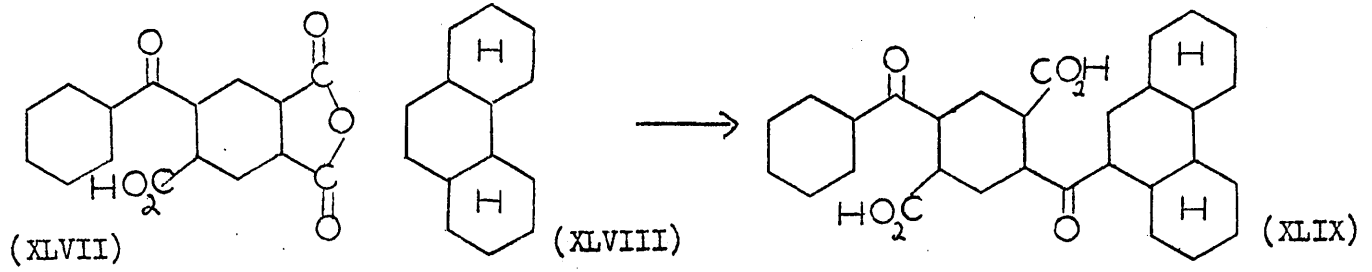
(XLV)



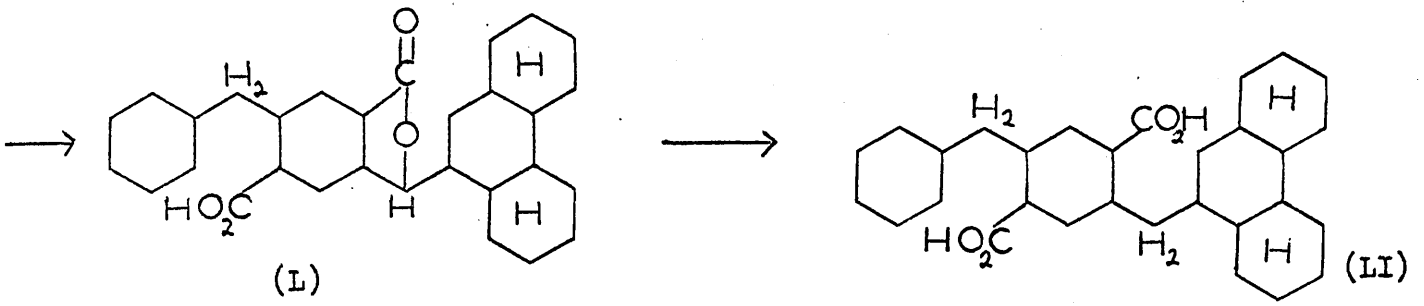
(XXXV)



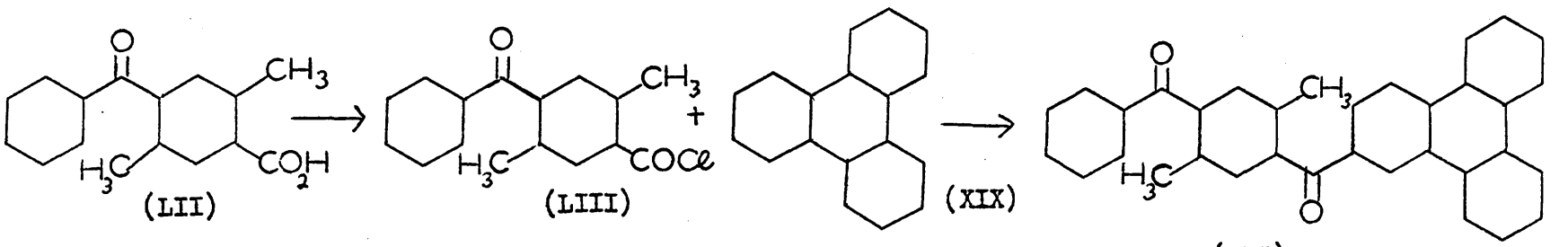
(XXIX)



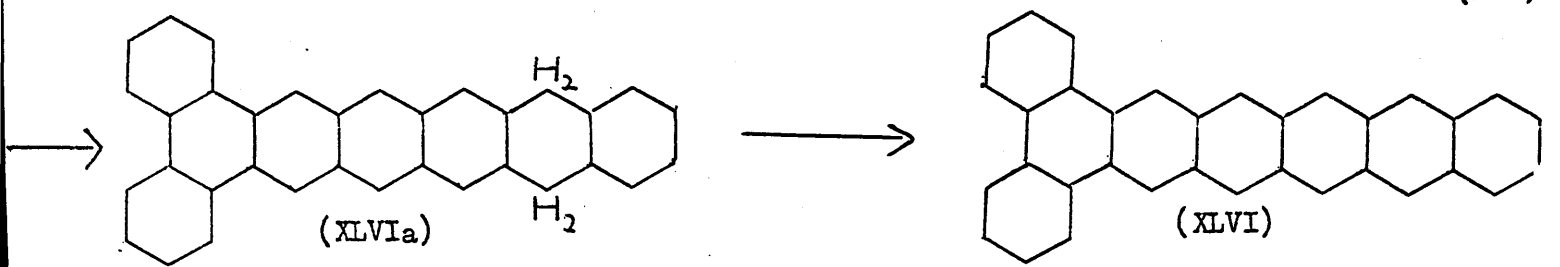
(XLVII) (XLVIII) (XLIX)



(L) (LI)



(LII) (LIII) (XIX) (LIV)



(XLVIa) (XLVI)

No trace of the required hydrotetrabenzheptacene (XVI) derivative could be found and it must be assumed that it was not stable at the temperature of the pyrolysis.

The attempted synthesis of 1,2:3,4-dibenzhexacene (XLVI) also made use of this pyrolysis method for the final stage. The condensation of benzophenone-tricarboxylic acid anhydride (XLVII) with octahydrophenanthrene, (XLVIII) gives the intermediate (XLIX), which has the required skeleton for cyclisation to dibenzopentacene.[21]

Friedel-Crafts reactions involving anhydrides generally give low yields and this is overcome by using large amounts of reagents, however this is not always possible. In order to improve the yield of the initial intermediate it was hoped to condense triphenylene (XIX) with the acid chloride (LIII) to give the ketone (LIV). Direct cyclisation and reduction of (LIV) by an Elbs reaction, although giving small yields would circumvent the additional stages (XLIX), (I), (LI) required to convert (XLIX) to the intermediate (LI) suitable for cyclisation and reduction.

Benzophenonetricarboxylic acid is readily obtained by oxidation of 5-benzoylpseudocumene, firstly with dil. nitric acid which oxidises one of the methyl groups. Further oxidation with alkaline potassium permanganate yields the required acid which is converted to the anhydride on melting.[22] It was hoped to isolate the mono

acid from the first oxidation stage, which should be mainly the isomer (LII) in analogy with the oxidation of durene which forms the 2,5-dimethylterephthalic acid.[23] Conversion to the acid chloride and Friedel-Crafts condensation with triphenylene would yield the intermediate ketone (LIV) suitable for cyclisation.

The crude acid, isolated from the nitric acid oxidation, was refluxed with thionyl chloride to give the acid chloride as a brown viscous liquid. The condensation product with triphenylene gave a small amount of the required ketone on recrystallisation but the bulk of the product remained as a gum. This was pyrolysed without further purification and yielded a considerable amount of triphenylene and a substituted tetracene derivative, on sublimation of the residue. Chromatography of the sublimate afforded a separation of the mixture but only a small amount of the tetracene derivative was isolated. The U.V. spectrum did indicate however that this product was a derivative of 1,2:3,4-dibenzotetracene and the shifts from the parent compound were of the order of magnitude for alkyl substituents.

However throughout the course of this work only small amounts of triphenylene were used for each reaction sequence and at this stage insufficient product was obtained for a dehydrogenation. Further work on this reaction sequence was therefore terminated due to insufficient time.

EXPERIMENTAL

2,5-Dimethylterephthaloyl chloride (XXXIV).

Prepared and purified as described on page 120 .

Di-2,5-(triphenyloyl-2-)-p-xylene (XXXV).

Triphenylene (4gm.) and the above acid chloride (2g.) were powdered together and added to 20 mls. of dry benzene. Finely powdered aluminium chloride (3 g.) was added in one portion with stirring and the mixture became orange-red. On raising the temperature to 50° a more vigorous reaction took place and hydrogen chloride was evolved. After 20 mins. at this temperature the reddish-brown melt was poured onto a mixture of dil. hydrochloric acid and ice forming a cream precipitate. The benzene was distilled off and the organic residue was dissolved in xylene. The xylene solution was washed with dil. ammonia, water, filtered and concentrated. The resulting crystalline product (3.4 g.) was filtered and dried. Recrystallisation of a sample from xylene yielded tiny white needles. m.pt. 307-310° which dissolved in concentrated sulphuric acid to produce an orange colour.

Found		C=89.68%, H=5.03%
$C_{46}H_{30}O_2$	requires	C=89.90%, H=4.88%

Pyrolysis of di-2,5-(triphenyloyl-2-)p-xylene (XXXV).

The finely powdered ketone (3.2 gm.) was pyrolysed in two portions by heating in a sublimation tube at 410° under an atmosphere of carbon dioxide. The molten ketone became darker and droplets of water condensed on the cooler areas of the tube along with a pale yellow gum which boiled off from the sublimation boat. Heating was maintained until no further moisture was evolved (30 mins.). The sublimation boat contained a dark brown residue and this was retained for sublimation. The yellow gum was removed from the tube with refluxing cyclohexane and xylene and the U.V. spectrum of the solution indicated a small amount of a substituted dibenzotetracene, unreacted ketone and some triphenylene. The brown residue was sublimed under a good vacuum yielding at 250-300° (10^{-4} m.m. Hg.) a further small amount of a yellow gum and at 370-410° an orange-yellow sublimate which crystallised. The temperature was raised to 500° without further sublimate. The tube was extracted with boiling xylene which readily dissolved the initial sublimate and the less soluble orange-yellow product was scraped from the tube and dried. Resublimation under good vacuum (10^{-4} m.m. Hg.) gave a pale yellow orange solid m.pt. 398-400° which dissolved slowly in concentrated sulphuric acid on heating to give a light tan colour. M.S. molecular ion $^{m}/_{e}$ 578 and 580.

Found	C=95.06%, H=4.85%
$C_{46}H_{28}$ requires	C=95.17%, H=4.83%

A sample was recrystallised from trichlorobenzene yielding pale yellow-orange needles which were used for a quantitative U.V. spectrum.

Found		C=95.43%, H=4.62%
$C_{46}H_{26}$	requires	C=95.50%, H=4.50%

Attempted dehydrogenation using copper powder

The hydrocarbon (10 mg.) was powdered intimately with active copper powder (0.5 gm.) and the mixture heated at 270-300° for 30 minutes under carbon dioxide: A vacuum was applied (10^{-4} m.m. Hg.) and the temperature raised quickly to 350° and more slowly to 500° An orange yellow sublimate formed at 400° and proved on U.V. examination to be unchanged starting material. Repetition of the above procedure at a higher temperature (400°) resulted in the decomposition of the hydrocarbon as no sublimate was observed. This evidence supports the assumption that the hydrocarbon is the fully aromatic tetrabenzheptaphene and not a hydroderivative.

2,4,5-Trimethylbenzophenone.

This was prepared by Friedel-Crafts condensation of benzoyl chloride and pseudo-cumene as described by Clar and Frömmel.

2,5-Dimethyl-4-benzoylbenzoic acid (LII).

The crude ketone (210 gm.) was refluxed for four days with a solution of 220ml. concentrated nitric acid (d =1.42) and 1000ml. of water until the pale yellow organic layer had sunk to the bottom of the flask. The acid solution was decanted and retained. The yellow orange gum was dissolved in dil. sodium hydroxide giving a wine red solution which was thoroughly extracted with ether to remove unreacted ketone. The resulting aqueous alkaline solution was acidified hot with conc. hydrochloric acid giving an orange gum. After boiling the gum with concentrated hydrochloric acid for an hour and triturating with benzene a pale brown crystalline solid was obtained (60gm.) Recrystallisation of a sample from dil. acetic acid gave small squat colourless prisms m.pt. 192-193° (Lit. 151-152° ??) which gave a sapphire blue solution with concentrated sulphuric acid.

Found		C=75.47%, H=5.51%
$C_{16}H_{14}O_3$	requires	C=75.58%, H=5.55%

2,5-Dimethy-4-benzoylbenzoyl chloride (LI).

The crude acid (40g.) was refluxed for two hours with thionyl chloride (120gm.) and a few drops pyridine. The resulting dark brown solution was vacuum distilled to remove excess thionyl chloride and benzene was added and this was also distilled over to remove final traces of thionyl chloride. The acid chloride could not be recrystallised and was used without further purification.

2-Benzoyl-5-(triphenyloyl-2-)p-xylene(LIV)

The crude acid chloride (7.5gm.) and powdered triphenylene (5gm) were dissolved in dry benzene (15ml.) at 35°. Finely powdered aluminium chloride (4gms.) was added in one portion with stirring and the temperature was raised to 55-60°. The initial green colour persisted throughout even with addition of further aluminium chloride (1gm.). The melt was decomposed with ice and dil. hydrochloric acid and the benzene distilled from the mixture. The organic residue was dissolved in xylene, washed with dil. ammonia and water, filtered and taken to dryness. Trituration with light petrol (60-80) afforded light brown solid (12gm.) which readily formed a gum on heating or on attempted recrystallisation. By triturating a sample with acetone, and recrystallising the resulting solid from xylene, small regular pale yellow squat prisms wereobtained m.pt. 254-256° which

gave a wine-red solution with concentrated sulphuric acid.

Found		C=87.84%, H=5.45%
$C_{34}H_{24}O_2$	requires	C=87.90%, H=5.21%

Pyrolysis of the ketone (LIV).

The crude mixture (6g.) was pyrolysed in two portions as described previously. After 30 mins. the residue from the pyrolysis was sublimed under good vacuum (10^{-4} m.m. Hg.) and gave a large amount of pale yellow sublimate between 200-300°. At higher temperatures 330°-370° a small amount of orange sublimate was obtained. No further sublimate occured up to 500°. The mixture of sublimates was dissolved in xylene and the U.V. spectrum indicated mainly triphenylene and a tetracene derivative. The extract was dried, concentrated, and chromatographed over Grade I alumina. Eluting with cyclohexane yielded an almost colourless first fraction containing triphenylene, and with benzene a series of fractions containing both the tetracene derivative and triphenylene. A small amount of orange product precipitated form the latter fractions and the solution in cyclohexane showed λ max. 4480 , 4200 , 3960 , 3200, 3060 Å which indicated an alkyl substituted dibenzotetracene, however insufficient product was available for dehydrogenation.

CHAPTER 6

RINGS CURRENTS - CORRELATION BETWEEN CALCULATED and OBSERVED CHEMICAL SHIFTS.

Introduction

It is generally found that the ring protons attached to benzene and other aromatic hydrocarbons are found at much lower field than ethylenic protons, although formally they have the same environment . This is due to a secondary magnetic field being generated by the circular motion of the π-electrons around closed conjugated paths within the molecule when placed in the applied field.[1] The new secondary field tends to reinforce the applied field at the position of the hydrogen atoms at the edge of the rings causing these aromatic protons to resonate at lower fields.[2]

Examination of the n.m.r. spectra of several polycyclic aromatic hydrocarbons and an application of this ring current model predicted the order in which the protons should appear in the spectrum, but did not give a satisfactory value for the shifts.[3] However a number of improvements have been made since this initial paper.

The simple π-electron current idea was replaced by a better model with two current loops not in the plane of the ring but above and below the molecular plane with a radius equal to that of the carbon-carbon bonds in benzene.[4,5] It was also realised that the ring currents are not all of the same magnitude but that each ring in the molecule has its own particular current.[6]

The theory was placed on a sounder basis using a quantum mechanical approach which allowed the relative magnitudes

of the ring currents to be calculated.[7] Further adaptation of this idea has been undertaken by several authors culminating in the McWeeny 'ring current' theory which allows the ring current of a particular ring and the secondary field generated at a particular proton to be calculated.[8]

Very recently this theory has been exhaustively investigated by Haigh, Mallion and Armour[9] who examined the n.m.r. spectra of a large number of polycyclic aromatic hydrocarbons in a common solvent. The observed shifts of the protons in these molecules were then compared with the calculated values from theoretical predictions which allowed the development of the simple relationship.

$$\tau_{obs.} = -1.56(H'/H'benzene)+4.34$$

where H'/H'benzene is the sigma ratio, or the ratio of the secondary field at the proton under consideration to that of a proton in benzene.[9] The accuracy of this method has been shown further by Mallion,[10] who has extended the calculations to larger molecules and found a similar agreement between calculated and observed chemical shifts.

However this can only be applied directly to non-hindered protons and the difference between calculated and observed shifts for sterically hindered protons is not good. Nevertheless a comparison of these hindered protons indicates a fairly

constant deviation of 0.62 p.p.m. between the observed and calculated shifts, and taking this factor into consideration most of the hindered protons can be treated in the normal manner.[9]

Apart from the obvious value of this method for calculating accurate chemical shifts of protons in polycyclic aromatic hydrocarbons, two trends emerge.[11] Firstly the ring currents are generally greater than that of benzene but fall off rapidly with increasing condensation to the particular ring in question.[11] Secondly the main contribution to the secondary field at any proton arises from the most adjacent rings. The contribution from any particular ring decreasing rapidly with distance from the proton concerned.[11]

In the work in this chapter, the n.m.r. spectra of several large polycyclic aromatic hydrocarbons have been obtained, using carbon disulphide as a solvent and the computer of average transients (C.A.T.), to overcome the low solubility exhibited by these highly condensed molecules. With particular interest in the bay protons, which are shifted to low fields with respect to other aromatic protons due to steric interactions, the observed chemical shifts have been compared with the recently calculated values.

In the following discussion it is hoped to show that there are some exceptions to the first trend mentioned above. Evidence which supports the second point, has been found on investigation of the shifts of the bay protons of several series of related

compounds, in which the chemical shift of protons in the same environment remains the same, or show small shifts to higher field when the additional rings are distant from these protons.

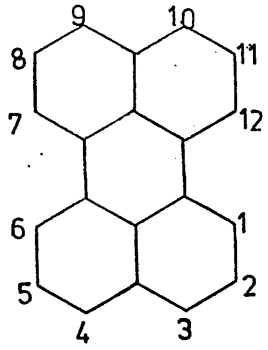
It is also hoped to indicate once more, that in many cases strict application of Robinsons aromatic sextet[12] to these aromatic hydrocarbons goes a long way to explaining the observed properties of these molecules.

Discussion

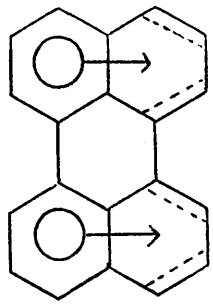
The most recent calculated chemical shifts[9] are of particular interest as they predict the unusually high field resonance of the bay protons H_1, H_6, H_7 and H_{12} of perylene (I) Table 1. The calculated ring current for the middle ring of perylene is 0.239, which is only a quarter of the value for benzene (unity) It is also found that the steric correction factor for these bay protons is 0.44 p.p.m. which is smaller than the average value 0.62 p.p.m. found for other molecules.[9]

Therefore a combination of these two factors offers further evidence for considering perylene as two naphthalene moities joined by virtually single bonds, as indicated by the x-ray analysis.[13] The high field resonance of the bay protons results from reduced steric interaction due to the long bond and the small ring current in the middle ring. The latter fact being indicated by magnetic anisotropy measurements[14] and by use of the aromatic sextets which allows only two sextets in the perylene molecule as shown (Ia).

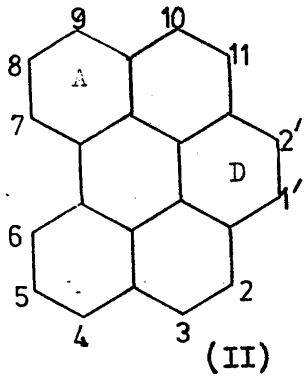
However this is not the case for 1:12-benzoperylene (II) in which the bay protons H_6 and H_7 are formally in the same environment yet resonate at much lower field (0.8 p.p.m. downfield from perylene).[15] The middle ring has been further condensed yet the calculated ring current[11] is 0.684 and although small in comparison with benzene is still three times that of perylene.



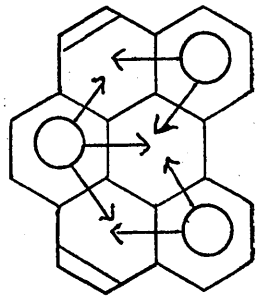
(I)



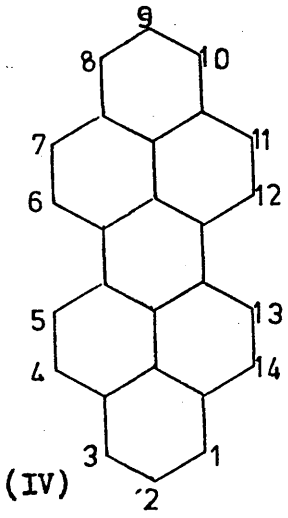
(Ia)



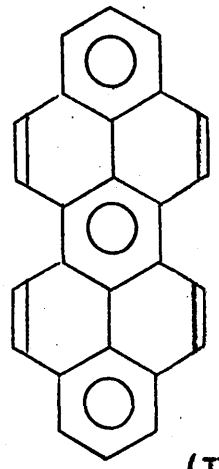
(II)



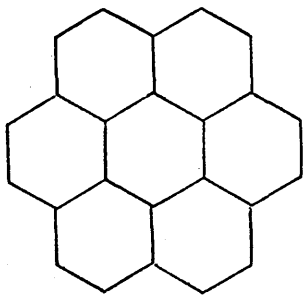
(II



(IV)



(IVa)



(V)

This example therefore appears to contradict the first trend.[11]

An explanation is offered by application of the sextet principle whereby the extra ring has introduced a third inherent sextet to the molecule with subsequent localisation of these three inherent sextets. This is also borne out by the calculated ring current intensities for these rings, A=1.292 and D=1.380, (II), the former being much greater than the corresponding value of 0.972 for ring A of perylene.

The x-ray structure analyses[12,16] of (I) and (II) also indicate that there should be more steric interaction between the bay protons of 1:12-benzoperylene as the central bond length is 1.48Å compared with 1.50Å in perylene. Both the experimental conditions and the theoretical predictions[17] for the relative ease of benzogenic diene addition of maleic anhydride to (I) and (II) indicate that the middle ring of (II) must have more benzenoid character than perylene.

One would therefore expect that the larger ring currents and steric interaction would result in the bay protons of (II) resonating at lower field than in perylene as is in fact the case.

Recent calculations[18] have shown that the ring current in the middle ring of peropyrene (IV) is 1.446 which is as high as the outer rings of coronene[9] (V). As in the case of 1:12-benzoperylene II this contradicts the trend whereby condensation to a ring diminishes the ring current contribution.[11]

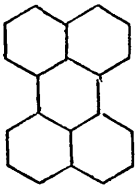
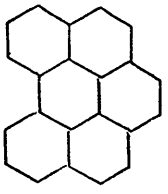
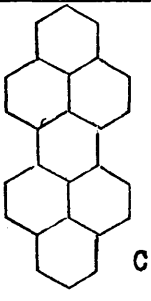
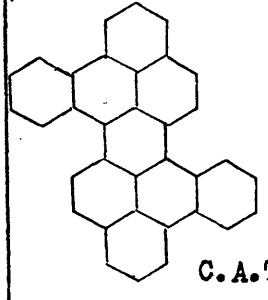
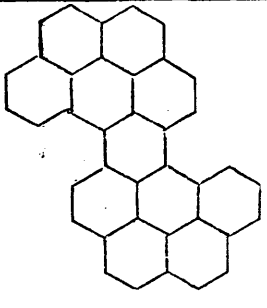
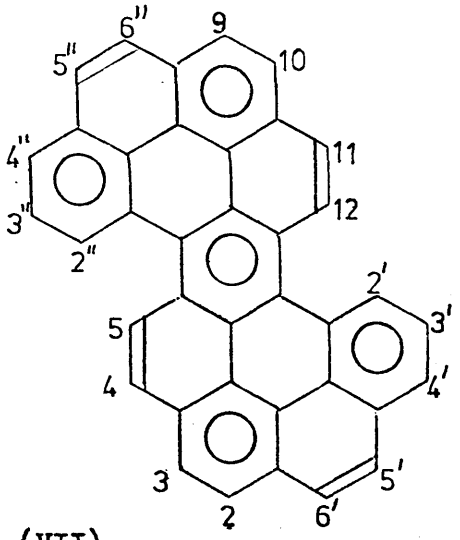
Compounds in CS_2 at 100 M.Hz	Aromatic proton shifts in Hz. exo T.M.S.			
	Bay protons	Obs.	Calc.	Other protons
	$H_{1,6,7,12}$ (d.d) J_o=7, J_m=1.2	805	811	$H_{3,4,9,10}$ 757(d.d) J_o=8.4, J_m=1.4 $H_{2,5,8,11}$ 735(d.d) $J_{2,3}$=8.7, $J_{1,2}$=7.6
	$H_{6,7}$ (d.d) J_o =7.5, J_m=1.4	882	896	$H_{1',2'}$ 819(s) $H_{3,10}$ 803 J_o=7.5, J_m=1.4 $H_{4,9}$ 796(s); $H_{2,8}$ 795(s); $H_{5,8}$ 788(t) J=7.5
 C.A.T.	$H_{5,6,12,13}$ (doublet) J=9.0	915	900	$H_{4,7,11,14}$ 832 (doublet) J= 9.0 $H_{1,3,5,8}$ 827 $H_{2,9}$ 825
 C.A.T.	$H_{6,13}$ (doublet) J=9.0 $H_{4',4''}$ (m)	905 838		$H_{3,10}$ 888(d.d.) J=7.5 $H_{1',1''}$ 882(m); $H_{1,8}$ 816 (d,d) J=7.5; $H_{7,14}$ 803 (doublet) J=9.0; $H_{2,9}$ 799 (t) J=7.5; $H_{2',2'',3',3''}$ 768(m)
 C.A.T.	$H_{5,12}$ (doublet) J=9.5 $H_{2',2''}$ (d.d) J_o=7.5 J_m=1.0	942 923		$H_{2,3,9,10}$ 843(s); $H_{4,12}$ 832(d.d) J=9.5 $H_{4',4''}$ 826(d.d) J=7.5 $H_{5',5''}$ 821(s); $H_{3',3''}$ 809 J=7.5

Table 1.

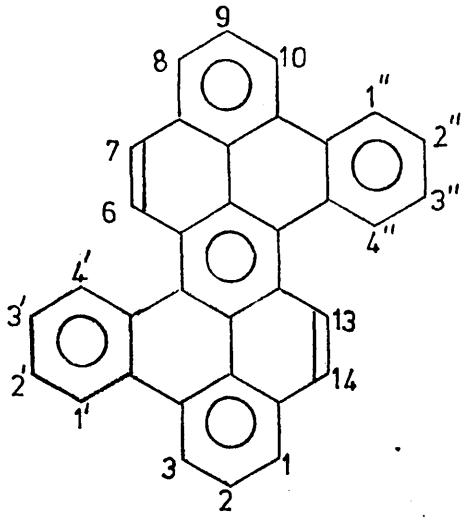
However this is readily explained by application of the aromatic sextet whereby peropyrene is best formulated with three inherent sextets, one of which is in the central ring as shown (IVa). Therefore one would expect a far larger ring current for this ring and subsequently the bay protons are calculated to be at lower field than the aforementioned bay protons of (I) and (II).

The observed spectrum of peropyrene shows a low field doublet at 915 Hz. due to protons H_5, H_6, H_{12}, H_{13} and with $J_{4,5}$ =9.5 Hz. Table 1. This confirms the calculated value and also provides further support for the sextet theory which not only predicts high benzenoid character for the three rings in peropyrene as shown, but a high degree of double bond character in the positions 4,5, 6,7, 11,12, 13,14, borne out by the large coupling constant of 9.5 Hz. It also explains why peropyrene does not react with maleic anhydride, exactly as predicted by M.O. calculations.[17]

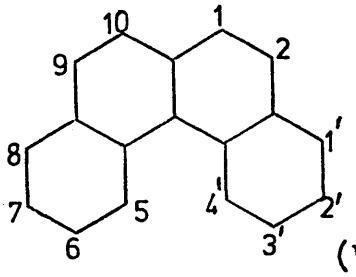
Although as yet, no calculations are available for comparison, the same situation is observed from the spectra of the symmetrical derivatives of peropyrene, compounds (VI) and (VII). Table 2. Once more coupling constants $J_{6,7}$ = $J_{13,14}$ =9.0Hz. in(VI) and $J_{4,5}$ = $J_{11,12}$ = 9.5Hz. in (VII) confirm a formulation for these molecules with the maximum number of sextets as shown. The coupling constants $J_{2',3'}$ = $J_{3',4'}$ = 7.5Hz. for ring A of (VI) are typical values for protons attached to an inherent sextet[15] Table 1.



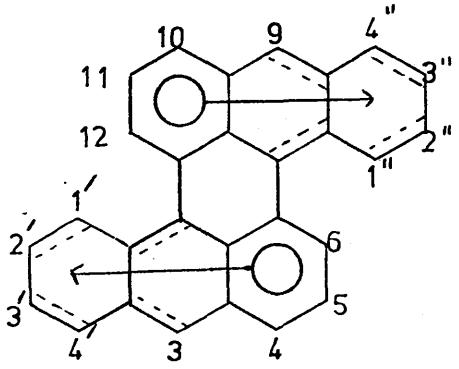
(VII)



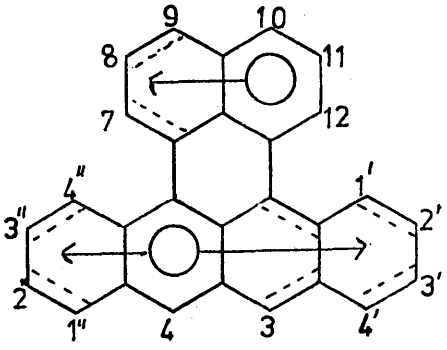
(VI)



(VIII)



(IX)



(X)

The bay protons H_6, H_{13} and $H_{4'}$, $H_{4''}$ of (VI) are not at as low field as the corresponding protons H_5, H_{12} and $H_{2'}$, $H_{2''}$ of (VII), although effectively in similar environments. In fact the bay protons H_6, H_{13} of (VI) are to high field of the protons H_5, H_{12} of peropyrane despite the fact that they are much more sterically hindered and can be considered as H α 4 protons (Martin terminology).[19]

Interactions between the H α 4 protons $H_{5'}$, H_4 of 3,4-benzophenanthrene (VIII) are sufficiently large to force the molecule into a non-planar configuration and these protons resonate at low field 888Hz.

The x-ray analysis[20] of (VII) shows that the molecule does adopt a distorted structure to alleviate these interactions, and although an x-ray analysis of (VI) has not been undertaken, this must also adopt a distorted structure to minimise interactions. As a result of this, one would be dealing with a non-coplanar molecule and this is thought to result in a loss of aromatic character and subsequently a reduction in the effective ring current. Although this is not the case for (VII), the molecule (VI) is less condensed and may be able to adopt a more distorted structure resulting in a loss of ring current.[21]

Therefore despite the fact that two linearly annellated rings have been added, introducing two new inherent sextets with

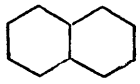
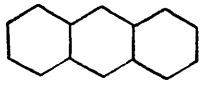
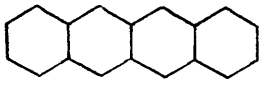
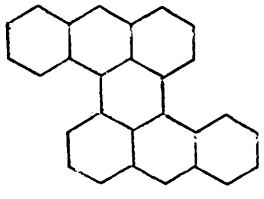
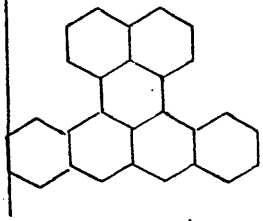
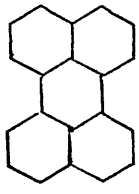
Compounds in CS_2 at 100 M. Hz.	Aromatic proton shifts in Hz. exo T.M.S.					
	Bay protons		Other protons			
			$H_{1,4,5,8}$	767		
			$H_{2,3,6,7}$	731		
			$H_{9,10}$	830		
			$H_{1,4,5,8}$	793		
			$H_{2,3,6,7}$	724		
			$H_{5,6,11,12}$	852		
			$H_{1,4,7,10}$	786		
			$H_{2,3,8,9}$	729		
	$H_{1',1''}$	872	$H_{3,9}$	819	$H_{5,11}$	750
	$H_{6,12}$	810	$H_{4',4''}$	794	$H_{2',3',3'',2''}$	730
			$H_{4,10}$	783		
	$H_{1',4''}$	860	$H_{3,4}$	832	$H_{8,11}$	754
	$H_{7,12}$	816	$H_{1'',4'}$	785	$H_{2',3',2'',3''}$	731
			$H_{9,10}$	774		
	$H_{1,6,7,12}$	805	$H_{3,4,9,10}$	757		
			$H_{2,5,8,11}$	735		

Table 2.

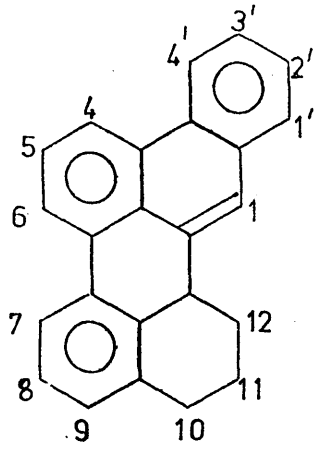
an increase in overcrowding at the bay positions, the protons in general have shifted to high field relative to peropyrene. In the light of (VII) this could only occur by diminished ring current in (VI) compared with both peropyrene (IV) and (VII).

A similar situation arises in the chemical shifts observed from the spectra of linear benzologues of perylene. The spectra of the two symmetrically substituted compounds, 1,2:7,8-dibenzoperylene(IX) and 1,2:5,6-dibenzoperylene (X) have been analysed and the results are shown in Table 2.

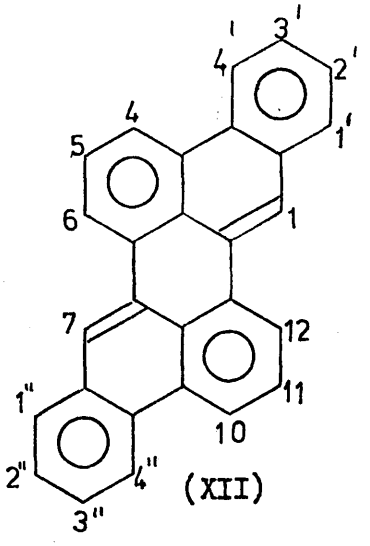
Once again despite the fact that the bay protons H_6,H_{12} of (IX) and H_7,H_{12} of (X) are in extremely overcrowded positions, they show only small shifts to low field compared to the corresponding protons in perylene. The other overcrowded protons H_1,H_1, and $H_{1'}$, $H_{4''}$ also resonate to high field of the corresponding protons in 3,4-benzophenanthrene.

The chemical shifts of the other unhindered protons in these molecules and in perylene itself are compared with the corresponding protons in naphthalene , anthracene and tetracene, and apart from the protons actually attached to the perylene part of the molecule, have almost identical chemical shifts as in the parent hydrocarbons Table 2.

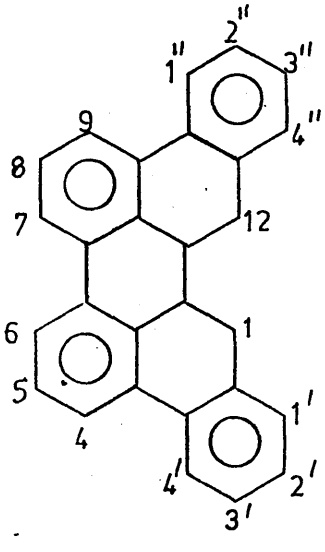
The shift to low field of the protons which are attached to the perylene part of the molecule relative to perylene indicate an increase in the ring current in these molecules. Yet the



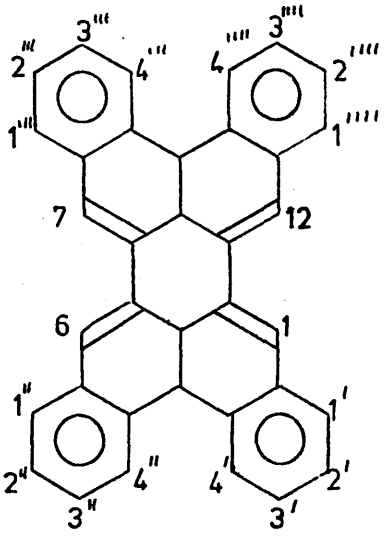
(XI)



(XII)



(XIII)



(XIV)

chemical shifts of the bay protons have hardly been altered despite the fact that they are further sterically hindered. In this case, however the long middle bonds will reduce the steric interaction and distortion of the molecule will occur more easily. Nevertheless the overall effect of linear annellation seems to have little effect on the bay protons in these three molecules (VI),(V),(X).

The spectra of the angularly annellated benzologues of perylene were also investigated in order to compare the effects of angular and linear annellation. Calculations of the ring current of 2,3-benzoperylene (XI) have already been published[11] and predict a very small ring current 0.236 for the middle ring. The spectra of (XII),(XIII) and (XIV) have been analysed and the results are shown in Table 3 along with the latest calculated values.[22] In each case the middle rings have a very small ring current and it seems reasonable to conclude that all the true perylene derivatives have this type of structure with low electron density and long bonds in the middle ring.

However despite the fact that the ring current in the middle rings are lower than the value for perylene, the bay protons are shifted to low field compared with the corresponding protons in perylene, even where they are in exactly analogous chemical environments (XIII).

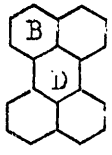
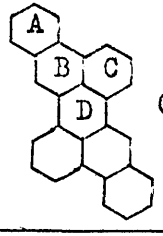
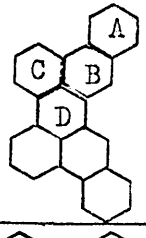
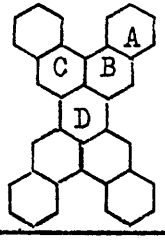
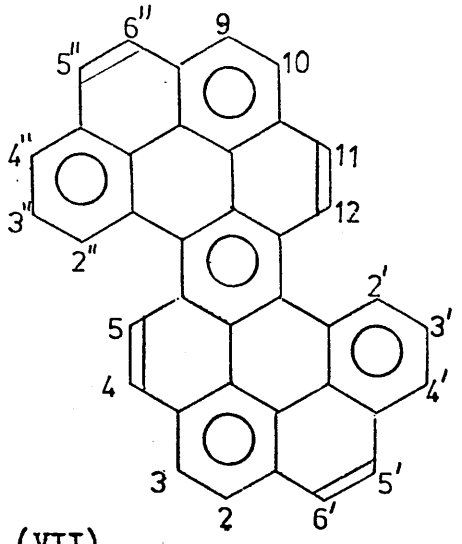
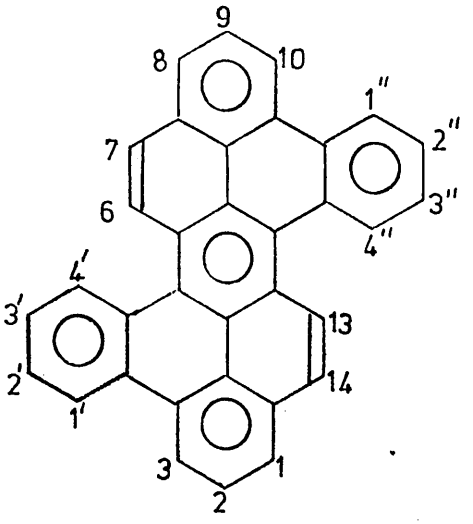
Compounds in CS_2 at 100 M.Hz.	'Ring current' intensities				Aromatic proton shifts in Hz. exo T.M.S.			
	A	B	C	D	Bay protons	Obs.	Calc.	Other protons
		0.972		0.239	$H_{1,6,7,12}$	805	811	$H_{3,4,9,10}$ 757 ; $H_{2,5,8,11}$ 735 .
 C.A.T.	1.078	0.877	1.041	0.232	$H_{1,7}$	837	832	$H_{4,10}$ 852; $H_{4',4''}$ 854; $H_{1',1''}$ 784; $H_{5,11}$ 769; $H_{2',3',2'',3''}$ 754.
					$H_{6,12}$	840 852	831	
 C.A.T.	1.077	0.876	1.043	0.233	$H_{1,12}$	854	836	$H_{4,10}$ 854 ; $H_{4',4''}$ 854 ; $H_{1',1''}$ 795 ; $H_{5,9}$ 752 ; $H_{2',2'',3',3''}$ 752.
					$H_{6,7}$	854	827	
 C.A.T.	1.101	0.996	0.996	0.214	$H_{1,6,7,12}$	872	864	$H_{1',1'',1''',1''''}$ 805; $H_{2',3',2'',3'',2''',3''',2'''',3''''}$ 757.
					$H_{4',4'',4''',4''''}$	891	——	

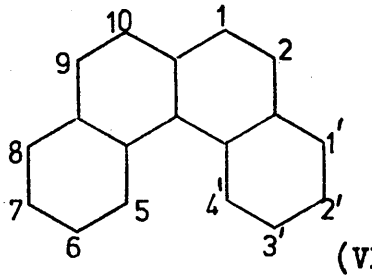
Table 3.



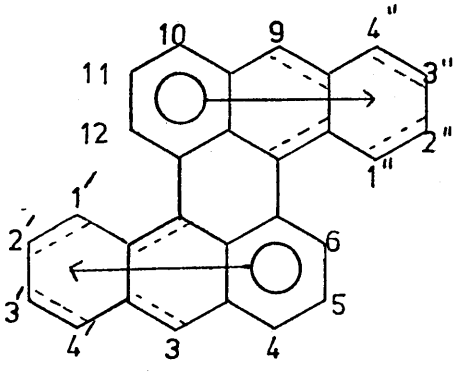
(VII)



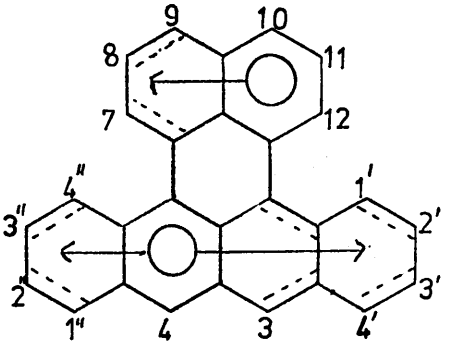
(VI)



(VIII)



(IX)



(X)

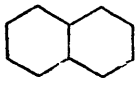
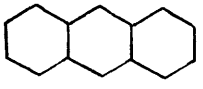
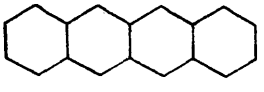
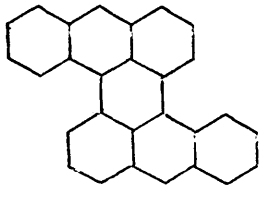
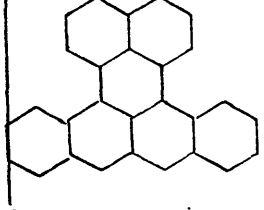
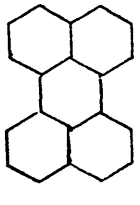
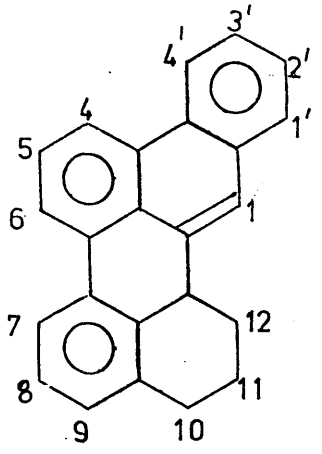
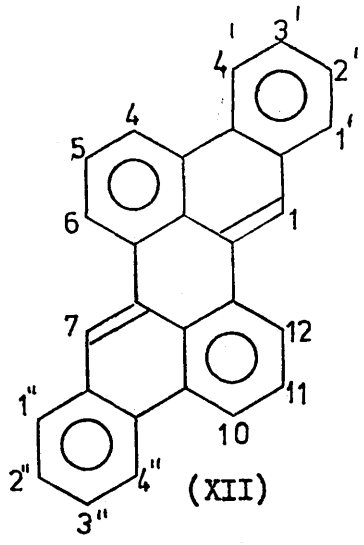
Compounds in CS_2 at 100 M. Hz.	Aromatic proton shifts in Hz. exo T.M.S.					
	Bay protons		Other protons			
			$H_{1,4,5,8}$	767		
			$H_{2,3,6,7}$	731		
			$H_{9,10}$	830		
			$H_{1,4,5,8}$	793		
			$H_{2,3,6,7}$	724		
			$H_{5,6,11,12}$	852		
			$H_{1,4,7,10}$	786		
			$H_{2,3,8,9}$	729		
	$H_{1',1''}$	872	$H_{3,9}$	819	$H_{5,11}$	750
	$H_{6,12}$	810	$H_{4',4''}$	794	$H_{2',3',3'',2''}$	730
			$H_{4,10}$	783		
	$H_{1',4''}$	860	$H_{3,4}$	832	$H_{8,11}$	754
	$H_{7,12}$	816	$H_{1'',4'}$	785	$H_{2',3',2'',3''}$	731
			$H_{9,10}$	774		
	$H_{1,6,7,12}$	805	$H_{3,4,9,10}$	757		
			$H_{2,5,8,11}$	735		

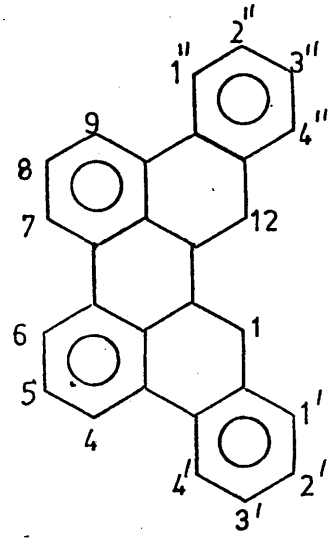
Table 2.



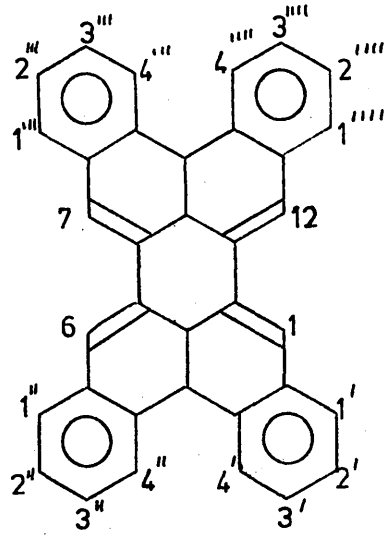
(XI)



(XII)



(XIII)



(XIV)

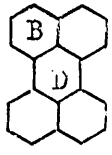
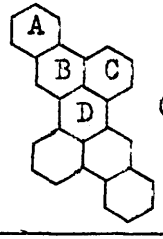
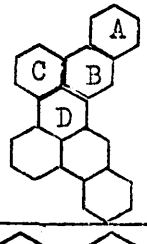
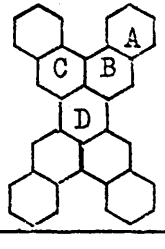
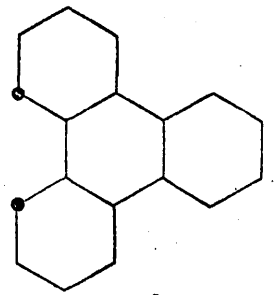
Compounds in CS_2 at 100 M.Hz.	'Ring current' intensities				Aromatic proton shifts in Hz. exo T.M.S.			
	A	B	C	D	Bay protons	Obs.	Calc.	Other protons
		0.972		0.239	$H_{1,6,7,12}$	805	811	$H_{3,4,9,10}$ 757 ; $H_{2,5,8,11}$ 735 .
 C.A.T.	1.078	0.877	1.041	0.232	$H_{1,7}$ $H_{6,12}$	837 840 852	832 831	$H_{4,10}$ 852; $H_{4',4''}$ 854; $H_{1',1''}$ 784; $H_{5,11}$ 769; $H_{2',3',2'',3''}$ 754.
 C.A.T.	1.077	0.876	1.043	0.233	$H_{1,12}$ $H_{6,7}$	854 854	836 827	$H_{4,10}$ 854 ; $H_{4',4''}$ 854 ; $H_{1',1''}$ 795 ; $H_{5,9}$ 752 ; $H_{2',2'',3',3''}$ 752.
 C.A.T.	1.101	0.996	0.996	0.214	$H_{1,6,7,12}$ $H_{4',4'',4''' 4''''}$	872 891	864 ——	$H_{1',1'',1''',1''''}$ 805; $H_{2',3',2'',3'',2''',3''',2'''',3''''}$ 757.

Table 3.

The angular addition of a ring also results in the formation of a new inherent sextet with a correspondingly high ring current in this ring. This is borne out by the calculations which indicate a high ring current for those rings which are also inherent sextets. Therefore the bay protons are found at lower fields than those of linearly annellated perylenes or perylene itself.

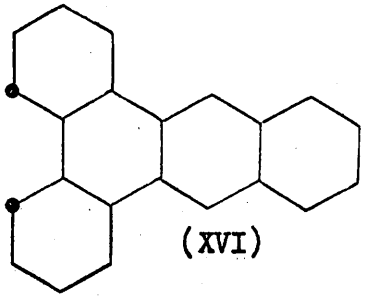
The spectrum of 2,3:4,5:8,9:10,11-tetrabenzoperylene (XIII) is also of interest as it confirms the assigned structure and has H$_{\alpha 4}$ protons at the 4',4",4''' and 4'''' positions. The observed chemical shift of these protons (891 Hz) is similar to the shift of the bay protons H$_5$, H$_{4'}$ of 3,4-benzophenanthrene (VIII) 888 Hz. The similar values indicate that the end rings of tetrabenzoperylene must be distorted out of the plane of the molecule as is the case for 3,4-benzophenanthrene. This also supports the deductions made from examination of the U.V. spectrum of (XIII), which showed characteristic broadening and a hypsochromic shift of the absorption maxima, but for which a quantitative measurement of the overcrowding could not be made as the α-bands were hidden by the more intense ρ-bands.

Finally, the interest in the bay protons of these aromatic hydrocarbons has led to the investigation of several more compounds whose n.m.r. spectra have hitherto not been analysed. In the series of several of these compounds (XV-XXIII) linear annellation of rings to the parent compound results in small shifts of the



(XV) bay proton 853

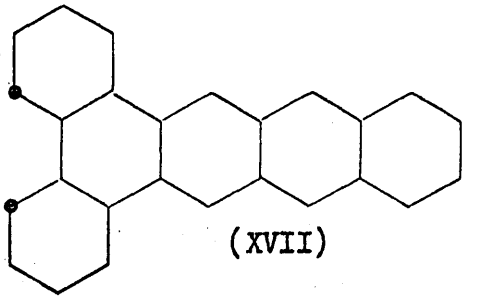
+9



(XVI)

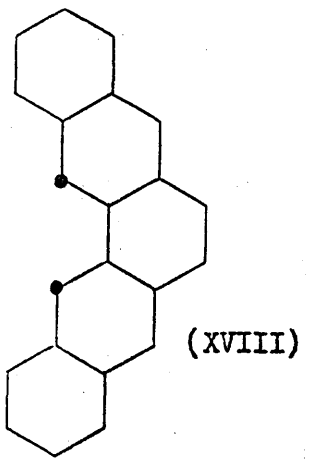
842

+5



(XVII)

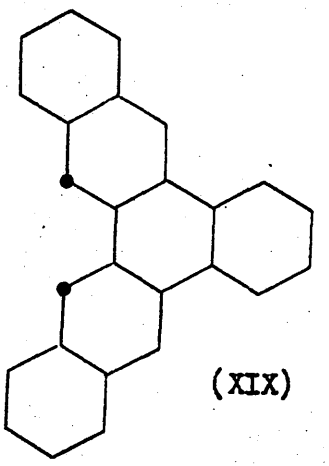
837 Hz. exo T.M.S.



(XVIII)

bay proton 907

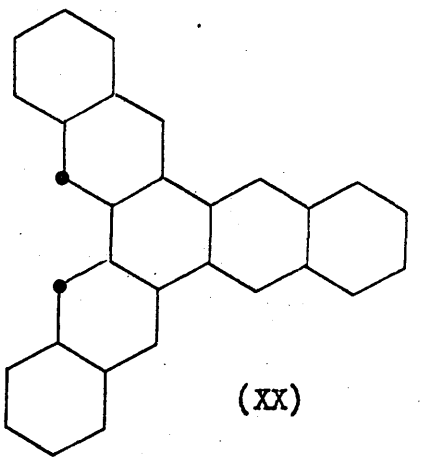
+ 6



(XIX)

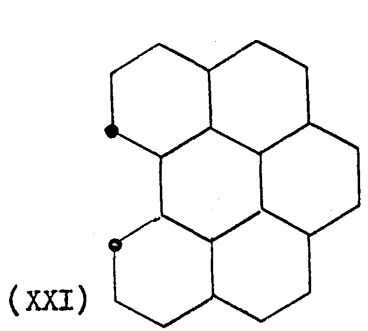
901

+ 7



(XX)

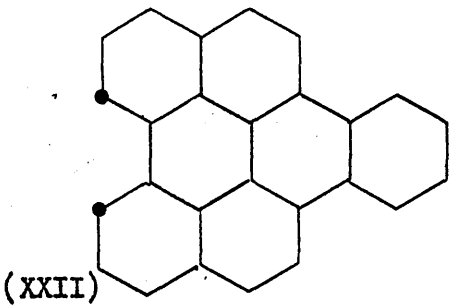
894 Hz. exo T.M.S.



(XXI)

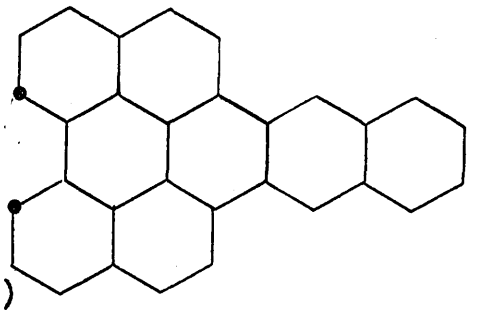
bay

• proton 882



(XXII)

+ 11 → 871



(XXIII)

+ 5 → 866 Hz. exo T.M.S.

bay protons to high field (marked with dots). This confirms that the main contribution to the secondary field at a given proton is from the immediately adjacent rings, the contribution from any particular ring falling of rapidly with distance from the proton concerned.

It is to be hoped that further calculations will be undertaken, as the n.m.r. spectra of many of these larger polycyclic aromatic hydrocarbons are now available and that techniques are being developed which enable spectra of even the very insoluble compounds to be run. This wealth of calculated and observed information can be compared with that amassed from the electronic absorption spectra and should lead to further insight into the electronic arrangement within these molecules.

BIBLIOGRAPHY

Chapter 1.

1) G.M. Badger, The Structure and Reactions of the Aromatic Compounds, Cambridge University Press, 1957, Chapt. 5.

2) J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, 1959, Chapt. 5.

3) F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York and London, 1969, p. 48, 148

4) A.A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc., 83, 231,(1961).

5) R.W. Fessenden and J.S. Waugh, J. Chem. Phys., 30, 944, (1959).

6) H. Rottendorf and S.Sternhell, Aust. J. Chem., 17, 1315, (1964).

7) E. Clar, B.A. McAndrew and M. Zander, Tet, 23, 985, (1967).

8) P. Durand, J. Parello, N.P. Buu-Hoi and L. Alais, Bull. Soc. Chim. Fr., 3, 2438, (1963).

9) E. Clar, A. McCallum and R.A. Robertson, Tet., 18, 1471, (1962); E. Clar, ibid., 2, 202, (1960).

10) E. Clar and A. Mullen, Tet., 24, 6719, (1968).

11) E. Clar and C.C. Mackay, Tet. Lett., 11, 871, (1970).

12) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, p. 38-39.

13) H. Akamatu and M. Kinoshita, Bull. Soc. Japan, 32, 774, (1959).

14) E. Clar, J.F. Guye-Vuilleme, A. McCallum and I.A MacPherson, Tet., 19, 2185, (1963); E.Clar, B.A. McAndrew and J.F. Stephen ibid, 26, 5465, (1970).

15) E.Clar, A. Mullen and, U.Sanigok, Tet., 25, 5639, (1969).

16) E. Clar, U.Sanigok and M.Zander, Tet., 24, 2817, (1968).

17) J.P. Wibaut and J. van Dijk, Rec. trav. Chim., 65, 412, (1946); L.W. Kampschmidt and J.P. Wibaut, Rec.trav. Chim., 73, 431, (1954).

18) E.Clar, B.A. McAndrew and U. Sanigok, Tet., 26, 2099, (1970).

19) S. Manmood Ali, K.K. Prasad, A.V.B. Sankaram and G.S. Sidhu, Tet. Lett., 25, 2305, (1971).

20) M.P. Williamson, R.J. Kostelnik and S.M. Castellano, J. Chem. Phys. 49, 2218, (1968).

21) D.J. Blears, S.S. Danyluk and T. Schaefer, Canad. J. Chem., 46, 654, (1968).

22) B.A. McAndrew, Ph.D. Thesis, Glasgow, 1967.

23) H.Vollmann, H. Becker, M. Correll and H. Streeck, Leibigs Ann., 531, 33, 59, 62, 72, (1937).

24) K. Tori and M. Ogata, Chem. Pharm. Bull. (Tokyo) , 12, 272, (1964).

25) J.A. Elridge and P.D. Ralph, J. Chem. Soc. (B), 249, (1966).

26) J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, 1959, p. 137.

27) S. Sternhell, Quart. Rev., 23, p. 236-270, (1969).

28) M.J.S. Dewar and R.C. Fahey, J.Am.Chem. Soc., 85, 2704, (1963).

29) P.M. Nair and G. Gopakumar, Tet. Lett., 13, 709, (1964).

30) P.M.E. Lewis, Tet. Lett., 21, 1859, (1971).

31) O. Jacobsen, Ber. dtsch. chem. Ges. 17, 2372, (1884).

32) P. Jannasch, ibid 10, 1357, (1877).

33) R. Fittig, W. Ahrens and L. Mattheides, Liebigs Ann., 147, 25, (1868).

34) M. Hübner and O.Wallach, Liebigs Ann., 154, 293, (1870).

35) A.K. Miller, J. Chem. Soc., 61, 1023, (1892).

36) J.B. Schoesmith and H. Rubli, J. Chem. Soc., 2, 3102, (1927).

37) G. Heller and K. Schulke, Ber. dtsch. chem. Ges., 41, 4635, (1908).

38) R.H. Mizzoni and P.E. Spoerri, J. Am. Chem. Soc., 76, 2201, (1954).

39) O. Poppenberg, Ber. dtsch. chem. Ges., 34, 3265, (1901).

40) C.G. Overberger, M.R. Byrd and R.B. Mesrobian, J. Am. Chem. Soc., 78, 1961, (1956).

41) E. Clar, Ber. dtsch. chem. Ges., 76, 609, (1943).

42) P.J. MacDonald, B.Sc. Thesis, Glasgow 1967.

43) K. Elbs and H. Eurich Ber. dtsch. chem. Ges. 20, 361, (1887).

44) R.D. Haworth and G. Sheldrick, J. Chem. Soc., 2, 1950 (1934).

45) O. Diels and K. Alder, Liebigs Ann., 486, 191, (1931).

46) O. Fischer and A. Sapper, J. Prakt. Chem., (2), 83, 205, (1911).

47) R.G. Jones And H. Gilman, Org. React., 6, 352, (1951).

48) V. Vesely and F. Stursa, Coll. Czec. Comm. 4, 21, (1932).

49) K. Ziegler and P. Tiemann, Ber. dtsch. chem. Ges. 85, 3410, (1952).

50) A. Claus, J. Prakt. Chem., 41, 409, (1890).

51) L. Gattermann, Liebigs Ann., 244, 53, (1888).

52) G.T. Morgan and E.A. Coulson, J. Chem. Soc., 2, 2323, (1931).

53) K. Auwers and A. Kockritz, Liebigs Ann., 352, 313, (1907).

54) W.H.Mills, J. Chem. Soc., 101, 2192, (1912).

Chapter 2

1) H. Rottendorf and S. Sternhell, Aust. J. Chem., 17, 1315, (1964).

2) E. Clar, B.A. McAndrew and M. Zander, Tet., 23, 985, (1967).

3) R.A. Hoffman, Molec. Phys. 1, 326, (1958); S. Sternhell, Quart. Rev., 23, p. 236-270, (1969).

4) S. Sternhell, Rev. Pure and Appl. Chem., 14, 15, (1964).

5) R.W. Crecely and J.H. Goldstein, Org. Mag. Res. 2, 613,(1970).

6) N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys. 36, 2443, (1962); J.B. Pawliczckand H. Guenther, Tet., 26, 1755, (1970).

7) E. Clar and J.W. Wrignt, Nature, Lond., 63, 921, (1949).

8) Nuclear Magnetic Resonance for Organic Chemists, Edited by D.W. Mathieson, Academic Press., 1967, Chapt. 8.

9) R.A. Hoffmann and S. Gronowitz, Arkiv for Kemi, 16, 471,(1960).

10) W. England and K. Ruendenberg, Theoret. Chim. Acta(Berl.) 22, 196, (1971).

11) C. Marschalk and C. Stumm, Bull. Soc. Chim. Fr., 15, 418, 777, (1948).

12) M. Martinoff, C.R. Acad. Sci., Paris, 238, 249, (1954).

13) L.F. Fieser and E.B. Herschberg J.Am.Chem.Soc., 62, 49,(1940). G.Wolf, J. Am. Che. Soc., 75, 2673, (1953).

14) N.P. Buu-Hoi and D. Lavit, Rec. Trav. Chim., 76, 200, (1957).

15) E. de.Barry Barnett and M.A. Matthews, Ber.dtsch.chem.Ges., 59, 1436, (1926).

16) A.Sieglitz and R. Marx, Ber.dtsch.chem.Ges., 56, 1619, (1923).

17) E.de. Barry Barnett and M.A. Matthews, J. Chem. Soc., 123, 2553, (1923).

Chapter 3

1) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. II, p. 250 and 254.

2) E. Clar, Ber. dtsch. chem. Ges., 76, 458, (1943).

3) F.C. Stehling and K.B. Bartz, J. Chem. Phys., 34, 1076, (1961); J.E. Bennet. Proc. Chem. Soc., 144, (1961).

4) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. II, p. 385.

5) E. Clar, ibid., Vol. II, p. 246-258.

6) A.H. Reddoch and D. H. Paskovich, Chem. Phys. Lett., 3, 351, (1969).

7) E. Clar, G. S. Fell, C.T. Ironside and A. Balsillie, Tet., 10, 26, (1960).

8) E. Clar, and D.G. Stewart, J. Am. Chem. Soc. 75, 2667, (1953).

9) E. Clar, W. Kelly, J. M. Robertson and M. G. Rossmann, J. Chem. Soc., 3878, (1956).

10) O.E. Polansky and G. Derflinger, Int. J. Quant. Chem., 379, (1967).

11) B.A. McAndrew, Ph.D. Thesis, Glasgow, 1967.

12) T.W. Armit and R. Robinson, J. Chem.Soc., 1604, (1924).

13) E. Clar, U. Sanigok and M. Zander, Tet., 24, 2817, (1968).

14) N. Jonathan, S. Gordon and B. P. Dailey, J. Chem. Phys., 36, 2443, (1962); R.H. Martin R. Flammang and M. Arabaoui, Bull. Soc. Chim. Belg., 74, 418, (1965).

15) E. Clar, Ber. dtsch. chem. Ges., 69, 152, (1936).

16) H. Vollmann, H. Becker, M. Corell and H. Streeck, Liebigs Ann., 531, 155, (1937).

17) R. Scholl and H. K. Meyer, Ber. dtsch. chem. Ges. 69, 152,(1936).

18) A. Lüttringhaus and H. Neresheimer, Liebigs Ann., 473, 259, (1929).

19) W. Bradley and F. K. Sutcliffe, J. Chem. Soc., 2119, (1951).

20) C.T. Ironside, Ph.D. Thesis, Glasgow, 1959.

Chapter 4

1) L. Pauling, The Chemical Bond, Cornell University Press, 1967, Chapt. 6.

2) C. A. Coulson, Valence, Oxford University Press, 1961, Chapt.4.

3) E. Clar, Aromatische Kohlenwasserstoffe, Springer-Verlag, 2nd Edition, 1952, p. 93, 461.

4) H.C. Longuett-Higgins, J. Chem.Phys,, 18, 265 (1950).

5) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, Vol. I. Chapt. 5.

6) P.S. Skell and R. J. Doerr, J.Am.Chem.Soc., 89, 4688, (1967).

7) E. Clar and D.G. Stewart, J.Am.Chem.Soc.,74, 2667, (1953).

8) E. Clar, I.A. MacPherson and H. Schultz-Kiesow, Liebigs Ann., 669,44, (1963).

9) L. Pauling, The Chemical Bond, Cornell University Press, 1967, p. 45.

10) O. Schmidt, Ber.dtsch.chem.Ges., 67, 1870,2078, (1934).

11) V.A. Izmail'ski, Chem. Abs. 43, 40, (1949).

12) E. Clar, W. Kemp and D.G. Stewart, Tet., 3, 325, (1958).

13) E. Clar, K.F.Lang and H. Schultz-Kiesow, Chem. Ber., 88, 1520, (1955).

14) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, Vol. I, Chapt. 5, p. 26.

15) R.L. Flurry Jr., Molecular Orbital Theories of Bonding in Organic Molecules, Arnold, 1968, Chapt. 4; M.J.S. Dewar and H.C. Longuett-Higgins, Proc.Roy. Soc. (London), A214, 482, (1952).

16) E. Clar and D.G. Stewart, J.Am.Chem.Soc., 76, 3504, (1953).

17) R. Scholl and K. Meyer, Ber.dtsch.chem.Ges., 65, 902, (1932), R.Scholl, K.Meyer and W. Winkler, Liebigs Ann., 494, 201, (1932).

18) R. Weisz and J. Korczyn, Ml.Chem., 45, 207, (1924).

19) E. Clar and D.G. Stewart, J.Chem.Soc., 3215, (1951).

20) P. Janasch, Zeit.für Chem., S.33,1871 : E. Schapauff, Ber. dtsch. chem. Ges. 19, 2510, (1886).

21) H. de Diesbach and V. Schmidt, Helv. Chim. Acta., 7, 644, (1924).

22) P.D. Bartlett and J.E. Jones, J. Am. Chem. Soc., 64, 1837, (1942).

23) W. Theilacker and M.L. Wessel-Ewald, Liebigs Ann., 594, 223, (1955).

24) I. Fleming and D.H. Williams, Spectroscopic Methods in Organic Chemistry, McGraw-Hill, Chapt. 3.

25) D.G. Stewart, Ph.D. Thesis, Glasgow, 1952.

26) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, Vol. I, p. 290.

Chapter 5.

1) A.E. Gillam and E.S. Stern, An Introduction to Electronic Absorption Spectroscopy, Arnold, 1954, Chapt. 8,9.

2) E. Clar, Ber. dtsch. chem. Ges. 69, 607, (1936).

3) J.R. Platt, J. Chem. Phys., 17, 484, (1949); J.R. Platt (Editor) Systematics of the Electronic Spectra of Conjugated molecules, Wiley, 1964.

4) H. Zimmermann and N. Joop, Zeit. für Electrochem., 65, 61,66, 138 (1961); E. Clar, C.T. Ironside and M. Zander, Tet., 22, 3527, (1966); E. Clar and B.A. McAndrew, future publication.

5) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. I, Chapt. 7.

6) E. Clar, Tet., 5, 98 (1959); 6, 355 (1959); 9, 202, (1960).

7) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. I, Chapt. 8.

8) E. Clar, ibid., Vol. I, p. 452, 461.

9) E. Clar, W. Kelly and W.G. Niven, J.Chem.Soc., 1833,(1956).

10) E. Clar and W. Kelly, J.Am.Chem.Soc., 76, 3502, (1954).

11) E. Phillipi, Mh.Chem. 32, 631 (1911); E. Clar, J.Chem.Soc., 2440, (1949).

12) E. Clar and M. Zander, J.Chem.Soc., 1577, (1958) ; I.G. Farbenindustrie A.G.,F.P. 857, 395/1939.

13) M. Zander, Chem.Ber., 92, 2744, (1959).

14) I.G. Farbenindustrie A.G. G.P. 590579, Chem. Zbl. 1934 11 3846; H.Waldmann, J. Prakt. Chem, (2) 150, 121, (1938).

15) B.A. McAndrew, Ph.D. Thesis, Glasgow, 1967.

16) H. de Diesbach and V. Schmidt., Helv. Chim. Acta. 7, 644, (1924).

17) E. Clar and C. Marschalk, Bull. Soc. Chim. Fr. 444, (1950).

18) L. Fieser, Organic Reactions, 1, 129, (1942).

19) J.W. Cook, J.Chem.Soc. 499,(1931); E. Clar and F. John, Ber.dtsch.chem.Ges., 64, 981, (1931); E. Clar, F. John and R. Avenarius, Ber.dtsch.chem.Ges., 72, 2139, (1939); L.F. Fieser and E. M. Dietz, Ber.dtsch.chem.Ges. 62, 1827, (1929).

20) E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964 Vol.I, p. 353.

21) E. Clar and H. Frömmel, Chem. Ber., 81, 163, (1948).

22) E. Clar, Ber.dtsch.chem.Ges., 81, 63, (1948).

23) P. Janasch, Zeit. für Chem. S. 33 1871; E. Schapauff, Ber. dtsch.chem. Ges., 19, 2570, (1886).

Chapter 6.

1) L. Pauling, J.Chem.Phys., 4, 673, (1936)

2) J.A. Pople, J.Chem.Phys., 24, 1111 (1956)

3) A.J. Bernstein, W.G. Schneider and J.A. Pople, Proc.Roy. Soc. (London) A236, 515 (1956).

4) J.S. Waugh and R.W. Fessenden, J.Am.Chem.Soc., 79, 846, (1957).

5) E. Johnson and F.A. Bovey, J.Chem.Phys., 29, 1012, (1958).

6) J.D. Memory, J.Chem.Phys., 38, 1341, (1963).

7) J.A. Pople, Molec.Phys., 1, 175, (1958).

8) R. McWeeny, Molec.Phys., 1, 311, (1958).

9) C.W. Haigh, R.B. Mallion, E.A.G. Armour, Molec.Phys., 18 737-766, (1970).

10) R.B. Mallion, J.Chem.Soc. (B), 681, (1971).

11) C.W. Haigh and R.B. Mallion, Molec.Phys., 18, 767, (1970).

12) T.W. Armit and R.Bobinson, J.Chem.Soc., 1604, (1924).

13) D.M.Donaldson, J.M. Robertson and J.G. White, Roc.Roy.Soc., A220, 311, (1953).

14) H. Akamatu and Y. Matsunaga, Bull.Chem.Soc. Japan, 26, 364, (1953); 29, 800, (1956).

15) E.Clar, U. Sanigok and M.Zander, Tet., 24, 2817, (1967).

16) J.G. White, J.Chem.Soc., 1398, (1948); J.Trotter, Acta,Cryst., 12, 889, (1959).

17) O.K. Polansky and G. Derflinger, Inter.J.Quant.Chem., 1, 379, (1967).

18) R.B. Mallion, J.Med.Chem. (in press).

19) R.H. Martin, Tet., 20, 897, (1964).

20) J.M. Robertson and J. Trotter, J.Chem.Soc. 2614, (1959).

21) C.W. Haigh and R.B. Mallion (unpublished results).

22) R.B. Mallion (private communication to Prof. Clar).

23) B.A. McAndrew, Ph.D. Thesis, Glasgow, 1967.

24) F.L. Hirshfield, S. Sandler and G.M. J. Schmidt, J.Chem.Soc., 2108, (1963).